

Supporting Information to

**Solvent-controlled photocatalytic divergent cyclization of alkynyl aldehydes: access to
cyclopentenones and dihydropyrans**

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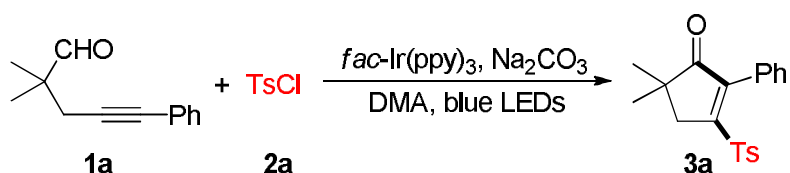
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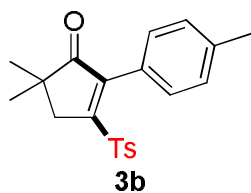
General. Unless otherwise noted, materials obtained from commercial suppliers were used directly without further purification. The substrates **1** are synthesized according to the reported methods.¹ ¹H, ¹³C, and ¹⁹F NMR spectra were measured on a 600 MHz NMR spectrometer using CDCl₃ or DMSO-d₆ as the solvent with tetramethylsilane (TMS) as the internal standard. The proton-decoupled ¹⁹F NMR spectroscopy was used to determine the ¹⁹F NMR data. Chemical shifts (δ) are given in parts per million relative to TMS, and the coupling constants are given in hertz. High-resolution mass spectrometry (HRMS) analysis were carried out using a TOF MS instrument with ESI source. Column chromatography was performed using silica gel (200-300 mesh).

General Procedure for the Synthesis of Cyclopentenones **3**

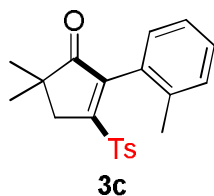


To a mixture of *fac*-Ir(ppy)₃ (2.6 mg, 0.004 mmol), Na₂CO₃ (42.4 mg, 0.4 mmol), H₂O (7.2 μ L, 0.4 mmol), and **2a** (57.0 mg, 0.3 mmol) in 2 mL of DMA was added **1a** (37.2 mg, 0.2 mmol) under a nitrogen atmosphere. After 5 h of irradiation at a distance of ~5 cm from 15 W blue LEDs (BESTLLON[®] lamps, 450 nm, 100% light intensity) at 25 °C, the reaction mixture was quenched with water, extracted with EtOAc, washed with brine, dried over anhydrous Na₂SO₄, and concentrated. Column chromatography on silica gel (petroleum ethers/EtOAc = 5:1) gave 52 mg (76% yield) of **3a** as a white solid; mp 112-113 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.47 (d, J = 8.2 Hz, 2H), 7.35 (t, J = 7.3 Hz, 1H), 7.31 (t, J = 7.3 Hz, 2H), 7.25-6.89 (m, 4H), 2.85 (s, 2H), 2.36 (s, 3H), 1.20 (s, 6H); ¹³C NMR (151 MHz, CDCl₃) δ 209.96, 162.72, 145.20, 143.81, 135.38, 129.55, 129.48, 129.02, 128.62, 128.15, 127.64, 44.44, 43.05, 24.74, 21.54; HRMS (ESI) m/z : [M + Na]⁺ Calcd for C₂₀H₂₀O₃SNa 363.1025; Found 363.1026.

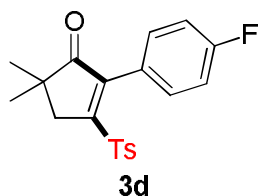
¹ X.-X. Peng, D. Wei, W.-J. Han, F. Chen, W. Yu and B. Han, *ACS Catal.*, 2017, **7**, 7830.



Compound 3b: 59 mg, 83% yield, white solid, mp 107-108 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 5:1; ^1H NMR (600 MHz, CDCl_3) δ 7.51 (d, J = 8.2 Hz, 2H), 7.17 (d, J = 8.1 Hz, 2H), 7.14 (d, J = 7.9 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 2.80 (s, 2H), 2.38 (s, 3H), 2.36 (s, 3H), 1.18 (s, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 210.15, 161.95, 145.17, 143.86, 139.18, 135.49, 129.56, 129.48, 128.38, 128.20, 125.63, 44.41, 43.06, 24.75, 21.55, 21.35; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{21}\text{H}_{22}\text{O}_3\text{SNa}$ 377.1182; Found 377.1185.

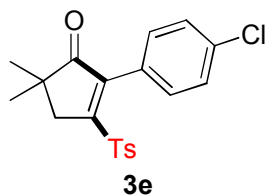


Compound 3c: 55 mg, 78% yield, white solid, mp 88-90 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 5:1; ^1H NMR (600 MHz, CDCl_3) δ 7.37 (d, J = 8.2 Hz, 2H), 7.22 (t, J = 7.5 Hz, 1H), 7.13 (d, J = 7.5 Hz, 1H), 7.10 (d, J = 8.2 Hz, 2H), 7.02 (d, J = 7.6 Hz, 1H), 6.91 (d, J = 7.5 Hz, 1H), 2.98 (s, 2H), 2.36 (s, 3H), 1.73 (s, 3H), 1.23 (d, J = 7.5 Hz, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 209.84, 163.91, 145.16, 144.99, 136.00, 135.16, 129.63, 129.52, 129.42, 128.93, 128.68, 128.21, 125.26, 44.44, 42.83, 25.44, 24.20, 21.55, 19.35; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{21}\text{H}_{22}\text{O}_3\text{SNa}$ 377.1182; Found 377.1186.

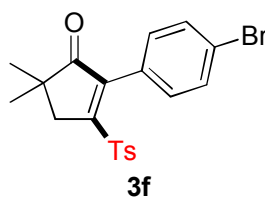


Compound 3d: 44 mg, 61% yield, white solid, mp 104-105 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 5:1; ^1H NMR (600 MHz, CDCl_3) δ 7.51 (d, J = 8.3 Hz, 2H), 7.26-7.10 (m, 4H), 7.03 (t, J = 8.6 Hz, 2H), 2.82 (s, 2H), 2.39 (s, 3H), 1.19 (s, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 209.92, 163.26 (d, J = 249.8 Hz), 162.90, 145.47, 142.68, 135.33, 131.74 (d, J = 8.5 Hz), 129.69, 128.16, 124.54 (d, J = 3.2 Hz), 114.86 (d, J = 21.8 Hz), 44.47, 43.15, 24.76,

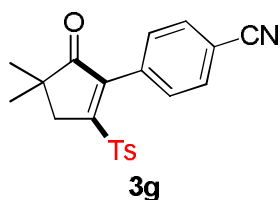
21.58; ^{19}F NMR (565 MHz, CDCl_3) δ -111.33; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{19}\text{FO}_3\text{SNa}$ 381.0931; Found 381.0934.



Compound 3e: 49 mg, 66% yield, white solid, mp 123-124 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 5:1; ^1H NMR (600 MHz, CDCl_3) δ 7.52 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 7.21 (d, J = 8.1 Hz, 2H), 7.15 (d, J = 8.4 Hz, 2H), 2.82 (s, 2H), 2.40 (s, 3H), 1.19 (s, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 209.69, 163.17, 145.61, 142.46, 135.39, 135.17, 131.00, 129.75, 128.22, 127.98, 127.02, 44.54, 43.10, 24.75, 21.61; HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{20}\text{ClO}_3\text{S}$ 375.0816; Found 375.0824.



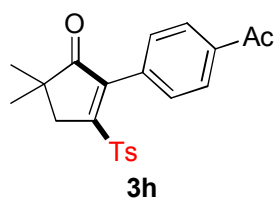
Compound 3f: 57 mg, 68% yield, white solid, mp 116-117 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 5:1; ^1H NMR (600 MHz, CDCl_3) δ 7.50 (d, J = 8.2 Hz, 2H), 7.44 (d, J = 8.3 Hz, 2H), 7.19 (d, J = 7.9 Hz, 2H), 7.06 (d, J = 8.5 Hz, 2H), 2.79 (s, 2H), 2.37 (s, 3H), 1.17 (s, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 209.53, 163.13, 145.58, 142.35, 135.02, 131.16, 130.84, 129.71, 128.16, 127.47, 123.58, 44.46, 42.99, 24.66, 21.55; HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{20}\text{BrO}_3\text{S}$ 419.0311; Found 419.0313.



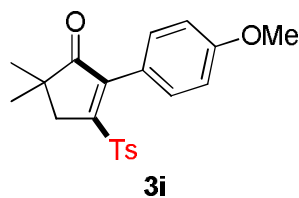
Compound 3g: 41 mg, 56% yield, white solid, mp 163-164 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 5:1; ^1H NMR (600 MHz, CDCl_3) δ 7.62 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 7.9 Hz, 2H), 7.32 (d, J = 7.9 Hz, 2H), 7.23 (d, J = 7.8 Hz, 2H), 2.78 (s, 2H), 2.39 (s,

3H), 1.18 (s, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 208.95, 164.25, 145.94, 141.74, 134.73, 133.51, 131.30, 130.34, 129.91, 128.19, 118.28, 112.65, 44.81, 43.14, 24.64, 21.57; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{21}\text{H}_{19}\text{NO}_3\text{SNa}$ 388.0978; Found 388.0978.

Crystal data for **3g** ($\text{C}_{21}\text{H}_{19}\text{NO}_3\text{S}$, 365.43): monoclinic, space group $P2_1/n$, $a = 5.8167(2)$ Å, $b = 17.2043(6)$ Å, $c = 19.0214(8)$ Å, $V = 1902.54(12)$ Å³, $Z = 4$, $T = 250.0$ K, $\mu = 0.190$ mm⁻¹, reflections collected 19469, independent reflections 4289 [$R_{\text{int}} = 0.0240$], refinement by full-matrix least-squares on F^2 , data/restraints/parameters 4289/0/238, goodness-of-fit on $F^2 = 1.115$, final R indices [$I > 2s(I)$] $R_1 = 0.0456$, $wR_2 = 0.1414$, R indices (all data) $R_1 = 0.0565$, $wR_2 = 0.1580$, largest diff peak and hole 0.31 and -0.37 e.Å⁻³. Crystallographic data for the structure of **3g** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 2060837.

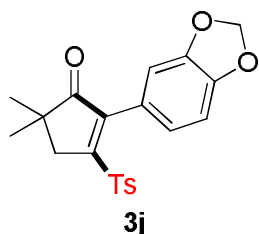


Compound 3h: 40 mg, 52% yield, yellow solid, mp 154-155 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 5:1; ^1H NMR (600 MHz, CDCl_3) δ 7.92 (d, $J = 8.3$ Hz, 2H), 7.52 (d, $J = 8.3$ Hz, 2H), 7.29 (d, $J = 8.3$ Hz, 2H), 7.20 (d, $J = 8.0$ Hz, 2H), 2.81 (s, 2H), 2.61 (s, 3H), 2.38 (s, 3H), 1.19 (s, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 209.41, 197.53, 163.60, 145.72, 142.84, 137.14, 135.09, 133.59, 129.86, 129.84, 128.27, 127.57, 44.78, 43.18, 26.65, 24.76, 21.63; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{22}\text{H}_{22}\text{O}_4\text{SNa}$ 405.1131; Found 405.1131.

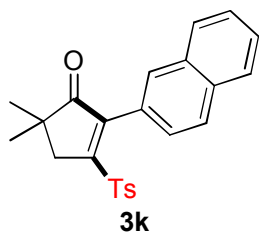


Compound 3i: 61 mg, 82% yield, white solid, mp 117-118 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 5:1; ^1H NMR (600 MHz, CDCl_3) δ 7.52 (d, $J = 8.2$ Hz, 2H), 7.20 (dd, $J = 14.0, 8.4$ Hz, 4H), 6.87 (t, $J = 5.7$ Hz, 2H), 3.83 (s, 3H), 2.79 (s, 2H), 2.38 (s, 3H), 1.18 (s, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 210.45, 161.36, 160.47, 145.18, 143.41, 135.59,

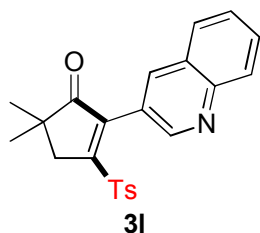
131.33, 129.61, 128.16, 120.74, 113.25, 55.25, 44.39, 43.17, 24.81, 21.61; HRMS (ESI) m/z : $[M + Na]^+$ Calcd for $C_{21}H_{22}O_4SNa$ 393.1131; Found 393.1135.



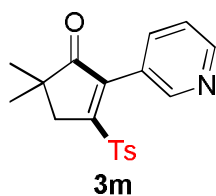
Compound 3j: 51 mg, 66% yield, yellow solid, mp 117-118 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 5:1; 1H NMR (600 MHz, $CDCl_3$) δ 7.54 (d, J = 8.3 Hz, 2H), 7.20 (d, J = 7.9 Hz, 2H), 6.77 (d, J = 8.0 Hz, 1H), 6.74 (dd, J = 8.0, 1.5 Hz, 1H), 6.62 (d, J = 1.2 Hz, 1H), 5.96 (s, 2H), 2.80 (s, 2H), 2.39 (s, 3H), 1.17 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 210.15, 162.13, 148.47, 147.06, 145.26, 143.13, 135.46, 129.57, 128.25, 124.22, 122.01, 109.95, 107.86, 101.22, 44.37, 42.98, 24.78, 21.59; HRMS (ESI) m/z : $[M + Na]^+$ Calcd for $C_{21}H_{20}O_5SNa$ 407.0924; Found 407.0927.



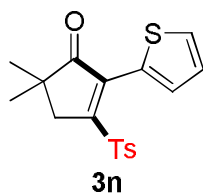
Compound 3k: 51 mg, 65% yield, white solid, mp 150-151 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 5:1; 1H NMR (600 MHz, $CDCl_3$) δ 7.82 (d, J = 7.3 Hz, 1H), 7.79-7.67 (m, 2H), 7.60 (s, 1H), 7.54-7.46 (m, 2H), 7.44 (d, J = 8.2 Hz, 2H), 7.22 (dd, J = 8.4, 1.5 Hz, 1H), 6.97 (d, J = 8.2 Hz, 2H), 2.93 (s, 2H), 2.21 (s, 3H), 1.25 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 210.16, 163.19, 145.27, 143.58, 135.27, 133.25, 132.42, 129.53, 129.44, 128.28, 128.26, 127.60, 127.29, 126.80, 126.49, 126.23, 126.12, 44.53, 42.99, 24.86, 21.43; HRMS (ESI) m/z : $[M + Na]^+$ Calcd for $C_{24}H_{22}O_3SNa$ 413.1182; Found 413.1182.



Compound 3l: 43 mg, 55% yield, yellow solid, mp 184-185 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 2:1; ^1H NMR (600 MHz, CDCl_3) δ 8.68 (d, J = 1.9 Hz, 1H), 8.11 (d, J = 8.5 Hz, 1H), 8.03 (d, J = 1.8 Hz, 1H), 7.80 (d, J = 8.1 Hz, 1H), 7.76 (dd, J = 8.3, 7.0 Hz, 1H), 7.58 (t, J = 7.5 Hz, 1H), 7.54 (d, J = 8.2 Hz, 2H), 7.09 (d, J = 8.2 Hz, 2H), 2.92 (s, 2H), 2.25 (s, 3H), 1.26 (s, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 209.64, 164.58, 149.80, 147.62, 145.82, 140.29, 137.28, 134.84, 130.37, 129.82, 129.15, 128.26, 128.16, 126.98, 126.73, 122.11, 44.77, 43.08, 24.82, 21.46; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{23}\text{H}_{21}\text{NO}_3\text{SNa}$ 414.1134; Found 414.1135.

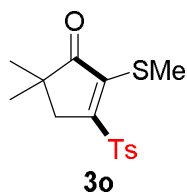


Compound 3m: 36 mg, 53% yield, yellow solid, mp 87-88 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 2:1; ^1H NMR (600 MHz, CDCl_3) δ 8.52 (d, J = 4.6 Hz, 1H), 8.35 (s, 1H), 7.51 (d, J = 7.8 Hz, 1H), 7.48 (d, J = 8.2 Hz, 2H), 7.22 (dd, J = 7.9, 4.7 Hz, 1H), 7.16 (d, J = 8.0 Hz, 2H), 2.77 (s, 2H), 2.32 (s, 3H), 1.13 (s, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 209.40, 164.40, 149.86, 149.64, 145.79, 140.45, 137.13, 134.94, 129.91, 128.18, 124.98, 122.50, 44.70, 43.20, 24.72, 21.60; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{19}\text{H}_{19}\text{NO}_3\text{SNa}$ 364.0978; Found 364.0982.

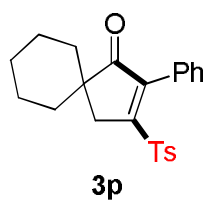


Compound 3n: 31 mg, 45% yield, white solid, mp 90-91°C; Flash column chromatography conditions: petroleum ethers/EtOAc = 5:1; ^1H NMR (600 MHz, CDCl_3) δ 7.88 (d, J = 3.6 Hz, 1H),

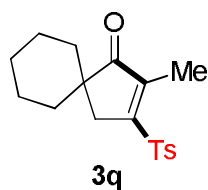
7.67 (d, $J = 8.2$ Hz, 2H), 7.55 (d, $J = 5.0$ Hz, 1H), 7.25 (d, $J = 8.1$ Hz, 2H), 7.17-7.05 (m, 1H), 2.79 (s, 2H), 2.40 (s, 3H), 1.18 (s, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 209.45, 158.69, 145.47, 136.09, 135.45, 133.20, 130.67, 129.78, 127.95, 127.87, 126.81, 44.20, 44.08, 24.88, 21.64; HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{19}\text{O}_3\text{S}_2$ 347.0770; Found 347.0778.



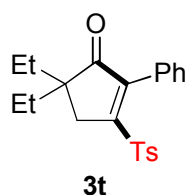
Compound 3o: 45 mg, 73% yield, yellow oil; Flash column chromatography conditions: petroleum ethers/EtOAc = 5:1; ^1H NMR (600 MHz, CDCl_3) δ 7.88 (d, $J = 7.3$ Hz, 2H), 7.36 (d, $J = 7.9$ Hz, 2H), 2.61 (s, 2H), 2.58 (s, 3H), 2.44 (s, 3H), 1.09 (s, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 207.99, 154.91, 145.57, 142.49, 135.68, 129.96, 127.98, 45.28, 42.75, 24.72, 21.70, 13.41; HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_{19}\text{O}_3\text{S}_2$ 311.0770; Found 311.0774.



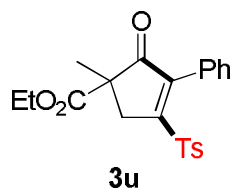
Compound 3p: 46 mg, 61% yield, white solid, mp 115-116°C; Flash column chromatography conditions: petroleum ethers/EtOAc = 5:1; ^1H NMR (600 MHz, CDCl_3) δ 7.44 (d, $J = 8.2$ Hz, 2H), 7.33 (t, $J = 7.4$ Hz, 1H), 7.28 (t, $J = 7.4$ Hz, 3H), 7.12 (dd, $J = 7.9, 2.1$ Hz, 4H), 2.91 (s, 2H), 2.35 (s, 3H), 1.78 (d, $J = 13.4$ Hz, 2H), 1.71 (d, $J = 12.5$ Hz, 1H), 1.66-1.58 (m, 2H), 1.41 (d, $J = 14.1$ Hz, 3H), 1.38-1.28 (m, 2H); ^{13}C NMR (151 MHz, CDCl_3) δ 209.95, 163.49, 145.12, 144.37, 135.46, 129.49, 129.47, 128.94, 128.58, 128.11, 127.63, 49.50, 39.76, 33.13, 24.89, 22.55, 21.55; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{23}\text{H}_{24}\text{O}_3\text{SNa}$ 403.1338; Found 403.1345.



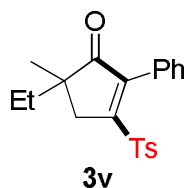
Compound 3q: 38 mg, 60% yield, colorless oil; Flash column chromatography conditions: petroleum ethers/EtOAc = 5:1; ^1H NMR (600 MHz, CDCl_3) δ 7.83 (d, J = 8.3 Hz, 2H), 7.40 (d, J = 8.1 Hz, 2H), 2.60 (q, J = 2.8 Hz, 2H), 2.47 (s, 3H), 2.08 (t, J = 2.3 Hz, 3H), 1.75-1.55 (m, 4H), 1.54-1.46 (m, 2H), 1.31-1.20 (m, 4H); ^{13}C NMR (151 MHz, CDCl_3) δ 211.79, 160.72, 145.59, 143.57, 136.10, 130.26, 127.95, 49.26, 39.55, 33.13, 24.95, 22.64, 21.76, 9.24; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{18}\text{H}_{22}\text{O}_3\text{SNa}$ 341.1182; Found 341.1193.



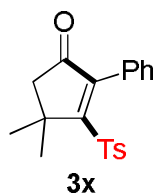
Compound 3t: 52 mg, 71% yield, white solid, mp 116-118 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 5:1; ^1H NMR (600 MHz, CDCl_3) δ 7.47 (d, J = 8.3 Hz, 2H), 7.35 (t, J = 7.4 Hz, 1H), 7.30 (t, J = 7.4 Hz, 2H), 7.22-7.09 (m, 4H), 2.84 (s, 2H), 2.36 (s, 3H), 1.65 (dq, J = 14.8, 7.4 Hz, 2H), 1.57 (dq, J = 14.7, 7.4 Hz, 2H), 0.75 (t, J = 7.4 Hz, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 210.59, 164.39, 146.10, 145.17, 135.49, 129.53, 129.40, 129.04, 128.52, 128.10, 127.66, 52.47, 37.34, 29.86, 21.58, 8.38; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{22}\text{H}_{24}\text{O}_3\text{SNa}$ 391.1338; Found 391.1342.



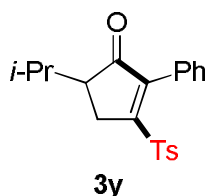
Compound 3u: 55 mg, 69% yield, colorless oil; Flash column chromatography conditions: petroleum ethers/EtOAc = 5:1; ^1H NMR (600 MHz, CDCl_3) δ 7.47 (d, J = 7.9 Hz, 2H), 7.37 (t, J = 7.4 Hz, 1H), 7.32 (t, J = 7.3 Hz, 2H), 7.15 (t, J = 8.3 Hz, 4H), 4.11 (q, J = 7.1 Hz, 2H), 3.46 (d, J = 18.6 Hz, 1H), 2.87 (d, J = 18.6 Hz, 1H), 2.36 (s, 3H), 1.48 (s, 3H), 1.16 (t, J = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 202.79, 170.06, 163.99, 145.44, 144.09, 135.19, 129.59, 129.53, 129.37, 128.19, 128.05, 127.76, 61.92, 54.61, 40.24, 21.57, 20.01, 13.86; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{22}\text{H}_{22}\text{O}_5\text{SNa}$ 421.1080; Found 421.1085.



Compound 3v: 51 mg, 72% yield, yellow solid, mp 73-74 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 5:1; ^1H NMR (600 MHz, CDCl_3) δ 7.47 (d, J = 8.3 Hz, 2H), 7.35 (t, J = 7.4 Hz, 1H), 7.31 (t, J = 7.4 Hz, 2H), 7.14 (dd, J = 8.0, 2.4 Hz, 4H), 2.84 (dd, J = 119.2, 18.8 Hz, 2H), 2.37 (s, 3H), 1.70-1.50 (m, 2H), 1.17 (s, 3H), 0.78 (t, J = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 210.36, 163.54, 145.21, 144.92, 135.45, 129.57, 129.48, 129.07, 128.58, 128.18, 127.70, 48.39, 40.23, 31.25, 23.08, 21.62, 8.72; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{21}\text{H}_{22}\text{O}_3\text{SNa}$ 377.1182; Found 377.1179.

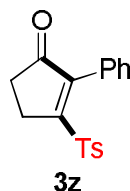


Compound 3x: 21 mg, 31% yield, white solid, mp 172-173 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 5:1; ^1H NMR (600 MHz, CDCl_3) δ 7.29 (t, J = 7.5 Hz, 1H), 7.21 (t, J = 7.7 Hz, 2H), 7.17 (d, J = 8.3 Hz, 2H), 6.95 (d, J = 8.1 Hz, 2H), 6.90 (d, J = 7.0 Hz, 2H), 2.63 (s, 2H), 2.30 (s, 3H), 1.78 (s, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 204.10, 173.25, 146.21, 144.40, 136.76, 129.29, 128.93, 128.69, 128.65, 127.74, 127.65, 53.28, 43.20, 27.77, 21.52; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{20}\text{O}_3\text{SNa}$ 363.1025; Found 363.1029.

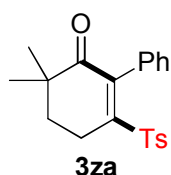


Compound 3y: 36 mg, 51% yield, white solid, mp 87-88 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 5:1; ^1H NMR (600 MHz, CDCl_3) δ 7.47 (d, J = 8.3 Hz, 2H), 7.35 (t, J = 7.4 Hz, 1H), 7.31 (t, J = 7.4 Hz, 2H), 7.14 (d, J = 8.1 Hz, 2H), 7.11 (d, J = 7.1 Hz, 2H), 3.03 (dd, J = 19.0, 7.1 Hz, 1H), 2.80 (dd, J = 19.0, 2.4 Hz, 1H), 2.63-2.61 (m, 1H), 2.37 (s, 3H), 2.33-2.28 (m, 1H), 1.01 (d, J = 6.9 Hz, 3H), 0.80 (d, J = 6.8 Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3)

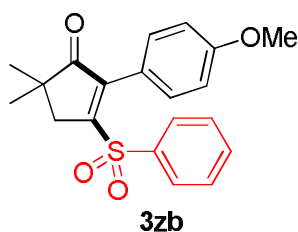
δ 207.69, 165.06, 146.56, 145.22, 135.50, 129.57, 129.41, 129.07, 128.46, 128.20, 127.72, 51.44, 29.76, 29.48, 21.61, 20.32, 17.19; HRMS (ESI) m/z : $[M + Na]^+$ Calcd for $C_{21}H_{22}O_3SNa$ 377.1182; Found 377.1181.



Compound 3z: 27 mg, 43% yield, white solid, mp 134-135 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 5:1; 1H NMR (600 MHz, $CDCl_3$) δ 7.48 (d, J = 8.3 Hz, 2H), 7.38-7.35 (m, 1H), 7.32 (t, J = 7.4 Hz, 2H), 7.14 (dd, J = 11.4, 4.6 Hz, 4H), 3.05-3.00 (m, 2H), 2.70-2.66 (m, 2H), 2.37 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 205.44, 165.75, 146.45, 145.32, 135.32, 129.59, 129.43, 129.11, 128.36, 128.32, 127.76, 34.49, 26.56, 21.59; HRMS (ESI) m/z : $[M + Na]^+$ Calcd for $C_{18}H_{16}O_3SNa$ 335.0712; Found 335.0717.

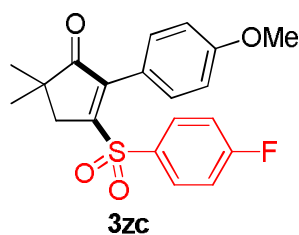


Compound 3za: 28 mg, 40% yield, white solid, mp 95-96 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 5:1; 1H NMR (600 MHz, $CDCl_3$) δ 7.26-7.21 (m, 3H), 7.16 (t, J = 7.6 Hz, 2H), 7.06 (d, J = 8.0 Hz, 2H), 6.78 (d, J = 7.2 Hz, 2H), 2.99 (t, J = 6.1 Hz, 2H), 2.36 (s, 3H), 2.03 (t, J = 6.1 Hz, 2H), 1.16 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 202.29, 153.91, 144.25, 140.86, 136.64, 132.23, 129.89, 129.31, 128.02, 127.77, 127.26, 40.81, 34.64, 23.73, 23.40, 21.57; HRMS (ESI) m/z : $[M + H]^+$ Calcd for $C_{21}H_{23}O_3S$ 355.1362; Found 355.1368.

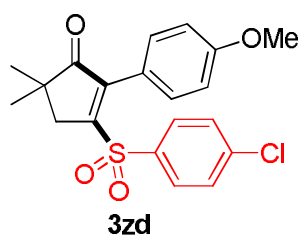


Compound 3zb: 62 mg, 87% yield, yellow solid, mp 103-104 °C; Flash column chromatography

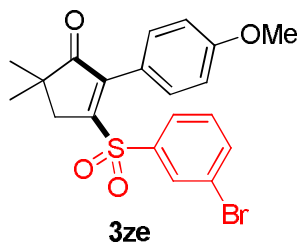
conditions: petroleum ethers/EtOAc = 5:1; ^1H NMR (600 MHz, CDCl_3) δ 7.62 (dd, J = 8.4, 1.1 Hz, 2H), 7.53 (t, J = 7.5 Hz, 1H), 7.37 (t, J = 7.9 Hz, 2H), 7.19 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 3.80 (s, 3H), 2.81 (s, 2H), 1.17 (s, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 210.28, 161.03, 160.46, 143.67, 138.48, 133.94, 131.26, 128.88, 128.00, 120.56, 113.24, 55.20, 44.37, 43.08, 24.74; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{20}\text{O}_4\text{SNa}$ 379.0975; Found 379.0978.



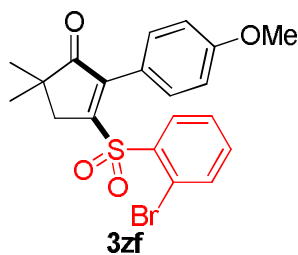
Compound 3zc: 53 mg, 71% yield, white solid, mp 123-124 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 5:1; ^1H NMR (600 MHz, CDCl_3) δ 7.66-7.58 (m, 2H), 7.16 (d, J = 8.7 Hz, 2H), 7.03 (t, J = 8.5 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H), 3.82 (s, 3H), 2.84 (s, 2H), 1.19 (s, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 210.13, 165.86 (d, J = 257.5 Hz), 160.84 (d, J = 71.5 Hz), 143.75, 134.59 (d, J = 3.0 Hz), 131.25, 130.98 (d, J = 9.7 Hz), 120.49, 116.21 (d, J = 22.8 Hz), 113.36, 55.27, 44.39, 43.03, 24.79; ^{19}F NMR (565 MHz, CDCl_3) δ -102.37; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{19}\text{FO}_4\text{SNa}$ 397.0880; Found 397.0885.



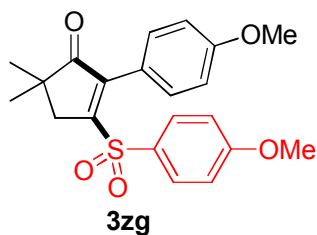
Compound 3zd: 51 mg, 66% yield, white solid, mp 105-107 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 5:1; ^1H NMR (600 MHz, CDCl_3) δ 7.52 (d, J = 8.6 Hz, 2H), 7.32 (d, J = 8.7 Hz, 2H), 7.15 (d, J = 8.7 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H), 3.82 (s, 3H), 2.84 (s, 2H), 1.19 (s, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 210.07, 160.86, 160.63, 143.91, 140.78, 137.01, 131.23, 129.51, 129.17, 120.44, 113.37, 55.28, 44.40, 42.97, 24.80; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{19}\text{ClO}_4\text{SNa}$ 413.0585; Found 413.0592.



Compound 3ze: 43 mg, 50% yield, white solid, mp 102-104 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 5:1; ^1H NMR (600 MHz, CDCl_3) δ 7.66-7.60 (m, 2H), 7.54-7.50 (m, 1H), 7.23 (t, J = 7.9 Hz, 1H), 7.12 (d, J = 8.8 Hz, 2H), 6.85 (d, J = 8.8 Hz, 2H), 3.83 (s, 3H), 2.89 (s, 2H), 1.22 (s, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 210.05, 160.98, 160.67, 144.19, 140.29, 136.86, 131.32, 131.14, 130.33, 126.43, 122.76, 120.23, 113.47, 55.27, 44.43, 42.88, 24.83; HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{20}\text{BrO}_4\text{S}$ 435.0260; Found 435.0265.

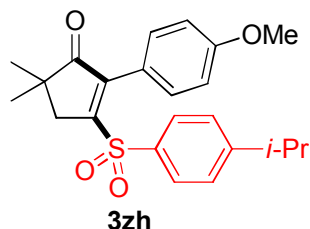


Compound 3zf: 45 mg, 52% yield, white solid, mp 104-104 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 5:1; ^1H NMR (600 MHz, CDCl_3) δ 7.83 (dd, J = 7.8, 1.7 Hz, 1H), 7.48 (dd, J = 7.8, 1.1 Hz, 1H), 7.24 (td, J = 7.6, 1.8 Hz, 1H), 7.19 (td, J = 7.7, 1.1 Hz, 1H), 7.06 (d, J = 8.8 Hz, 2H), 6.65 (d, J = 8.8 Hz, 2H), 3.73 (s, 3H), 3.06 (s, 2H), 1.29 (s, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 210.33, 160.37, 160.34, 143.29, 137.77, 134.62, 134.46, 132.05, 130.76, 127.19, 120.53, 120.36, 113.21, 55.26, 44.22, 42.29, 24.91; HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{20}\text{BrO}_4\text{S}$ 435.0260; Found 435.0265.

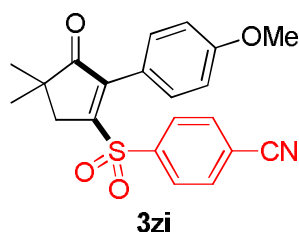


Compound 3zg: 54 mg, 70% yield, white solid, mp 130-131 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 5:1; ^1H NMR (600 MHz, CDCl_3) δ 7.54 (d, J = 8.9 Hz, 2H),

7.19 (d, $J = 8.7$ Hz, 2H), 6.86 (d, $J = 8.7$ Hz, 2H), 6.83 (d, $J = 8.9$ Hz, 2H), 3.81 (s, 6H), 2.79 (s, 2H), 1.17 (s, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 210.48, 164.00, 161.82, 160.38, 143.00, 131.28, 130.38, 129.85, 120.80, 114.18, 113.24, 55.62, 55.22, 44.32, 43.11, 24.79; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{21}\text{H}_{22}\text{O}_5\text{SNa}$ 409.1080; Found 409.1083.

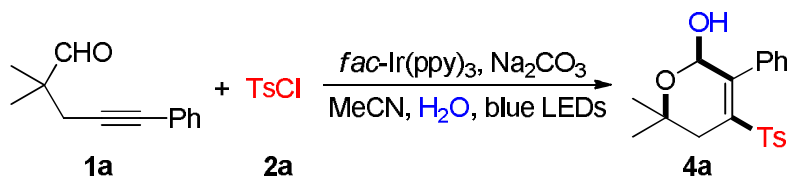


Compound 3zh: 64 mg, 80% yield, white solid, mp 93-95 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 5:1; ^1H NMR (600 MHz, CDCl_3) δ 7.53 (d, $J = 8.4$ Hz, 2H), 7.20 (d, $J = 8.3$ Hz, 2H), 7.15 (d, $J = 8.8$ Hz, 2H), 6.82 (d, $J = 8.8$ Hz, 2H), 3.81 (s, 3H), 2.91 (dt, $J = 13.8, 6.9$ Hz, 1H), 2.84 (s, 1H), 1.21 (d, $J = 6.9$ Hz, 6H), 1.19 (s, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 210.45, 161.62, 160.38, 155.74, 143.24, 135.71, 131.25, 128.33, 126.98, 120.74, 113.24, 55.21, 44.36, 42.99, 34.20, 24.84, 23.48; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{23}\text{H}_{26}\text{O}_4\text{SNa}$ 421.1444; Found 421.1448.

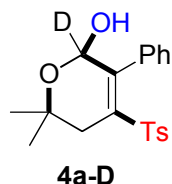


Compound 3zi: 34 mg, 45% yield, white solid, mp 113-114 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 5:1; ^1H NMR (600 MHz, CDCl_3) δ 7.68 (d, $J = 8.4$ Hz, 2H), 7.62 (d, $J = 8.4$ Hz, 2H), 7.12 (d, $J = 8.7$ Hz, 2H), 6.84 (d, $J = 8.7$ Hz, 2H), 3.83 (s, 3H), 2.89 (s, 2H), 1.22 (s, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 209.71, 160.90, 160.01, 144.70, 142.78, 132.45, 131.31, 128.66, 120.15, 117.55, 116.88, 113.52, 55.36, 44.53, 42.91, 24.84; HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{20}\text{NO}_4\text{S}$ 382.1108; Found 382.1110.

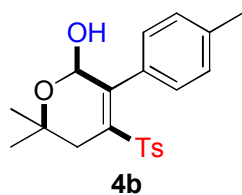
General Procedure for the Synthesis of Dihydropyransols 4



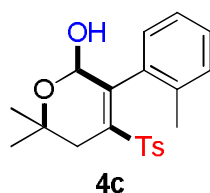
To a mixture of *fac*-Ir(ppy)₃ (2.6 mg, 0.004 mmol), Na₂CO₃ (42.4 mg, 0.4 mmol), H₂O (7.2 μL, 0.4 mmol) and **2a** (57.0 mg, 0.3 mmol) in 2 mL of dry MeCN was added **1a** (37.2 mg, 0.2 mmol) under a nitrogen atmosphere. After 5 h of irradiation at a distance of ~5 cm from 15 W blue LEDs (BESTLLON[®] lamps, 450 nm, 100% light intensity) at 50 °C, the reaction mixture was concentrated and column chromatography on silica gel (petroleum ethers/EtOAc = 3:1) gave 52 mg (73% yield) of **4a** as a colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 7.30 (s, 1H), 7.29-7.27 (m, 2H), 7.23 (t, *J* = 7.6 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.07-6.88 (m, 2H), 5.41 (d, *J* = 4.6 Hz, 1H), 2.85 (d, *J* = 5.2 Hz, 1H), δ 2.70 (dd, *J* = 17.6, 0.6 Hz, 1H), 2.54 (dd, *J* = 17.6, 1.6 Hz, 1H), 2.37 (s, 3H), 1.42 (s, 3H), 1.34 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 144.61, 143.94, 137.65, 137.16, 134.54, 129.23, 128.02, 127.72, 127.63, 92.55, 72.10, 36.18, 28.28, 27.63, 21.52; HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₂₀H₂₂O₄SNa 381.1131; Found 381.1131.



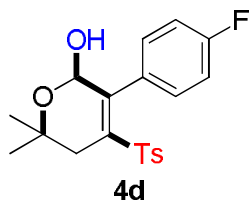
Compound 4a-D: The title compound was obtained from **1a-D** (>98% D) using the general procedure in 75% yield (54 mg) as a colorless oil, >98% D; Flash column chromatography conditions: petroleum ethers/EtOAc = 3:1; ¹H NMR (400 MHz, CDCl₃) δ 7.32 (s, 1H), 7.31–7.27 (m, 2H), 7.25 (d, *J* = 7.9 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.08–6.89 (m, 2H), 2.72 (d, *J* = 17.5 Hz, 1H), 2.63 (s, 1H), 2.55 (d, *J* = 17.5 Hz, 1H), 2.38 (s, 3H), 1.44 (s, 3H), 1.37 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 144.58, 144.03, 137.83, 137.25, 134.62, 129.31, 128.13, 127.82, 127.75, 92.31 (t, *J* = 21.0 Hz), 72.13, 36.27, 28.45, 27.69, 21.60; HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₂₀H₂₁DO₄SNa 382.1194; Found 382.1193.



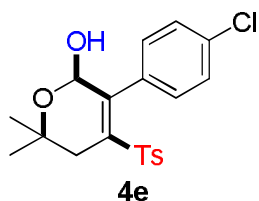
Compound 4b: 51 mg, 69% yield, colorless oil; Flash column chromatography conditions: petroleum ethers/EtOAc = 3:1; ^1H NMR (600 MHz, CDCl_3) δ 7.33 (d, J = 8.2 Hz, 2H), 7.11 (d, J = 8.1 Hz, 2H), 7.05 (d, J = 7.9 Hz, 2H), 6.96-6.82 (m, 2H), 5.40 (d, J = 4.8 Hz, 1H), 2.82 (d, J = 5.2 Hz, 1H), 2.68 (d, J = 17.5 Hz, 1H), 2.51 (d, J = 17.5 Hz, 1H), 2.38 (s, 3H), 2.34 (s, 3H), 1.41 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 144.69, 143.92, 137.91, 137.40, 137.21, 131.58, 129.14, 128.37, 127.78, 92.62, 72.06, 36.24, 28.27, 27.61, 21.53, 21.28; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{21}\text{H}_{24}\text{O}_4\text{SNa}$ 395.1288; Found 395.1276.



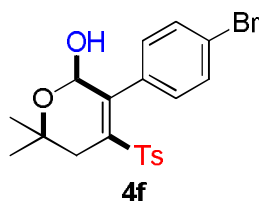
Compound 4c: 50 mg, 67% yield, colorless oil; Flash column chromatography conditions: petroleum ethers/EtOAc = 3:1; 1:1 mixture of two atropisomers; ^1H NMR (600 MHz, CDCl_3) δ 7.35 (d, J = 8.2 Hz, 1H), 7.32 (d, J = 8.2 Hz, 1H), 7.21 (d, J = 5.1 Hz, 1H), 7.19 (d, J = 4.7 Hz, 1H), 7.15 (t, J = 8.6 Hz, 2H), 7.11 (t, J = 7.4 Hz, 1H), 7.06 (d, J = 7.6 Hz, 0.5H), 7.01 (t, J = 7.2 Hz, 0.5H), 6.96 (d, J = 7.5 Hz, 0.5H), 6.56 (d, J = 7.6 Hz, 0.5H), 5.42-5.32 (m, 1H), 2.80 (d, J = 17.4 Hz, 0.5H), 2.68 (s, 1H), 2.64-2.60 (m, 1H), 2.40 (s, 3H), 2.39 (s, 0.5H), 2.34 (s, 1.5H), 1.98 (s, 1.5H), 1.50 (s, 1.5H), 1.42 (s, 1.5H), 1.38 (s, 1.5H), 1.34 (s, 1.5H); ^{13}C NMR (151 MHz, CDCl_3) δ 144.69, 144.21, 144.18, 143.81, 138.51, 137.66, 137.14, 137.07, 136.99, 135.29, 134.70, 133.43, 130.36, 129.81, 129.69, 129.39, 129.31, 128.38, 128.03, 127.99, 127.85, 126.83, 124.98, 124.94, 94.08, 90.86, 72.13, 72.12, 36.24, 36.09, 28.88, 28.42, 27.99, 27.59, 21.58, 20.66, 19.58; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{21}\text{H}_{24}\text{O}_4\text{SNa}$ 395.1288; Found 395.1276.



Compound 4d: 52 mg, 69% yield, white solid, mp 167-168 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 3:1; ^1H NMR (600 MHz, CDCl_3) δ 7.31 (d, J = 8.2 Hz, 2H), 7.14 (d, J = 8.1 Hz, 2H), 7.04-6.94 (m, 2H), 6.92 (t, J = 8.5 Hz, 2H), 5.39 (d, J = 4.9 Hz, 1H), 2.78-2.73 (m, 1H), 2.71 (d, J = 17.6 Hz, 1H), 2.55 (s, 1H), 2.39 (s, 3H), 1.42 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 162.56 (d, J = 248.0 Hz), 143.92 (d, J = 88.4 Hz), 138.47, 137.17, 130.36 (d, J = 3.4 Hz), 129.31, 127.67, 114.73 (d, J = 21.6 Hz), 92.48, 72.12, 36.27, 28.31, 27.65, 21.56; ^{19}F NMR (565 MHz, CDCl_3) δ -113.29; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{21}\text{FO}_4\text{SNa}$ 399.1037; Found 399.1033.

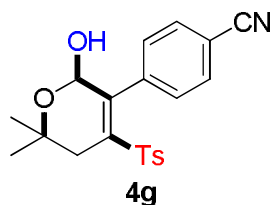


Compound 4e: 55 mg, 70% yield, white solid, mp 134-136 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 3:1; ^1H NMR (600 MHz, CDCl_3) δ 7.33 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.2 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 7.00-6.89 (m, 2H), 5.39 (d, J = 4.4 Hz, 1H), 2.75-2.72 (m, 1H), 2.69 (d, J = 17.6 Hz, 1H), 2.52 (d, J = 17.6 Hz, 1H), 2.40 (s, 3H), 1.42 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 144.35, 143.26, 138.47, 136.99, 134.28, 133.03, 129.36, 127.89, 127.76, 92.36, 72.11, 36.16, 28.34, 27.62, 21.59; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{21}\text{ClO}_4\text{SNa}$ 415.0741; Found 415.0735.

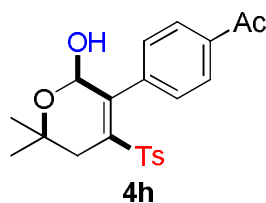


Compound 4f: 67 mg, 77% yield, white solid, mp 119-121 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 3:1; ^1H NMR (600 MHz, CDCl_3) δ 7.36 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 7.16 (d, J = 8.1 Hz, 2H), 6.88 (s, 2H), 5.38 (d, J = 4.7 Hz, 1H), 2.74-2.80

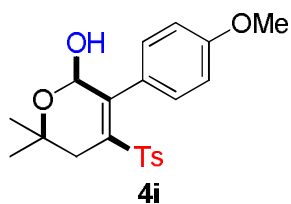
(m, 1H), 2.69 (d, $J = 17.6$ Hz, 1H), 2.52 (d, $J = 17.4$ Hz, 1H), 2.40 (s, 3H), 1.41 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 144.36, 143.20, 138.45, 136.95, 133.54, 130.81, 129.37, 127.76, 122.48, 92.28, 72.10, 36.12, 28.33, 27.62, 21.60; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{21}\text{BrO}_4\text{SNa}$ 459.0236; Found 459.0228.



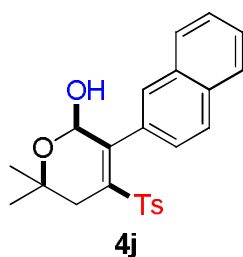
Compound 4g: 54 mg, 70% yield, white solid, mp 165-166 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 3:1; ^1H NMR (600 MHz, DMSO) δ 7.76 (d, $J = 8.2$ Hz, 2H), 7.45 (d, $J = 8.2$ Hz, 2H), 7.37 (d, $J = 8.1$ Hz, 2H), 7.28 (d, $J = 7.8$ Hz, 2H), 6.65 (d, $J = 6.8$ Hz, 1H), 5.32 (d, $J = 6.6$ Hz, 1H), 2.46 (d, $J = 17.3$ Hz, 1H), 2.40 (s, 3H), 2.33 (d, $J = 17.3$ Hz, 1H), 1.30 (s, 3H), 1.24 (s, 3H); ^{13}C NMR (151 MHz, DMSO) δ 145.05, 144.58, 141.21, 136.51, 135.99, 131.10, 129.90, 127.55, 118.92, 110.25, 91.21, 71.05, 35.65, 27.72, 27.35, 21.19; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{21}\text{H}_{21}\text{NO}_4\text{SNa}$ 406.1083; Found 406.1074.



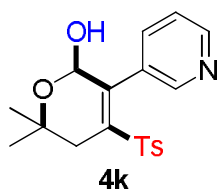
Compound 4h: 61 mg, 76% yield, white solid, mp 140-141 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 3:1; ^1H NMR (600 MHz, CDCl_3) δ 7.84 (d, $J = 8.6$ Hz, 2H), 7.36 (d, $J = 8.2$ Hz, 2H), 7.15 (d, $J = 8.0$ Hz, 2H), 7.23-7.05 (m, 2H), 5.42 (d, $J = 5.0$ Hz, 1H), 3.17 (d, $J = 5.3$ Hz, 1H), 2.63 (d, $J = 17.5$ Hz, 1H), 2.59 (s, 3H), 2.46 (dd, $J = 17.5, 1.3$ Hz, 1H), 2.39 (s, 3H), 1.39 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 197.70, 144.53, 143.64, 140.10, 137.77, 136.68, 136.29, 129.48, 127.79, 127.53, 92.21, 72.06, 36.08, 28.20, 27.59, 26.58, 21.56; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{22}\text{H}_{24}\text{O}_5\text{SNa}$ 423.1237; Found 423.1236.



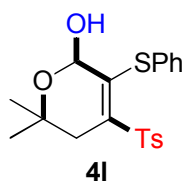
Compound 4i: 33 mg, 43% yield, colorless oil; Flash column chromatography conditions: petroleum ethers/EtOAc = 3:1; ^1H NMR (600 MHz, CDCl_3) δ 7.30 (d, J = 8.3 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 6.97-6.86 (m, 2H), 6.76 (d, J = 8.9 Hz, 2H), 5.40 (d, J = 4.6 Hz, 1H), 3.80 (s, 3H), 2.76 (d, J = 5.1 Hz, 1H), 2.72 (dd, J = 17.6, 0.7 Hz, 1H), 2.54 (dd, J = 17.6, 1.6 Hz, 1H), 2.37 (s, 3H), 1.42 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 159.47, 144.45, 143.86, 137.85, 137.32, 129.15, 127.67, 126.49, 113.19, 92.63, 72.08, 55.21, 36.33, 28.36, 27.64, 21.55; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{21}\text{H}_{24}\text{O}_5\text{SNa}$ 411.1237; Found 411.1229.



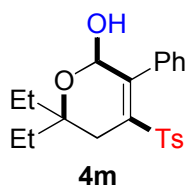
Compound 4j: 47 mg, 58% yield, yellow solid, mp 169-170 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 3:1; ^1H NMR (600 MHz, CDCl_3) δ 7.80 (d, J = 7.6 Hz, 1H), 7.80-7.59 (m, 2H), 7.53-7.44 (m, 2H), 7.37-7.28 (m, 1H), 7.19 (d, J = 8.1 Hz, 2H), 7.15-7.01 (m, 1H), 6.87 (d, J = 8.0 Hz, 2H), 5.50 (s, 1H), 2.97-2.83 (m, 1H), 2.79 (d, J = 17.6 Hz, 1H), 2.62 (d, J = 17.6 Hz, 1H), 2.25 (s, 3H), 1.47 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 144.35, 143.96, 138.41, 137.13, 132.67, 132.45, 129.00, 127.92, 127.69, 127.62, 127.20, 126.39, 126.14, 92.56, 72.17, 36.11, 28.39, 27.66, 21.40; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{24}\text{H}_{24}\text{O}_4\text{SNa}$ 431.1288; Found 431.1281.



Compound 4k: 25 mg, 35% yield, yellow solid, mp 166-167 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 1:1; ^1H NMR (600 MHz, CDCl_3) δ 8.45-8.40 (m, 1H), 8.06-7.99 (m, 1H), 7.54-7.46 (m, 1H), 7.33 (d, J = 8.2 Hz, 2H), 7.24-7.19 (m, 1H), 7.18 (d, J = 8.0 Hz, 2H), 5.38 (s, 1H), 2.67 (d, J = 17.5 Hz, 1H), 2.51 (d, J = 17.5 Hz, 1H), 2.39 (s, 3H), 1.42 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 148.41, 144.68, 141.77, 139.15, 136.77, 129.64, 127.65, 122.64, 92.09, 72.01, 36.20, 27.85, 27.82, 21.60; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{19}\text{H}_{21}\text{NO}_4\text{SNa}$ 382.1083; Found 382.1076.

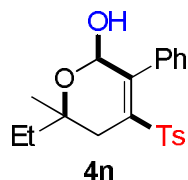


Compound 4l: 45 mg, 58% yield, yellow solid, mp 125-126 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 3:1; ^1H NMR (600 MHz, CDCl_3) δ 7.96 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 7.28 (t, J = 7.4 Hz, 1H), 7.22 (t, J = 7.6 Hz, 2H), 7.14 (d, J = 7.4 Hz, 2H), 4.91 (d, J = 4.9 Hz, 1H), 3.00-2.92 (m, 1H), 2.81 (d, J = 17.4 Hz, 1H), 2.53 (d, J = 17.4 Hz, 1H), 2.45 (s, 3H), 1.28 (s, 3H), 1.13 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 144.66, 143.17, 137.21, 136.24, 134.33, 129.88, 129.47, 129.09, 128.14, 89.46, 72.58, 38.04, 28.47, 28.15, 21.64; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{22}\text{O}_4\text{S}_2\text{Na}$ 413.0852; Found 413.0861.

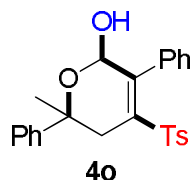


Compound 4m: 63 mg, 82% yield, colorless oil; Flash column chromatography conditions: petroleum ethers/EtOAc = 3:1; ^1H NMR (600 MHz, CDCl_3) δ 7.32 (d, J = 8.2 Hz, 2H), 7.28 (d, J = 7.4 Hz, 1H), 7.24 (t, J = 7.6 Hz, 2H), 7.11 (d, J = 8.1 Hz, 2H), 7.07-6.93 (m, 2H), 5.41 (d, J = 5.3 Hz, 1H), 2.69 (dd, J = 17.6, 0.7 Hz, 1H), 2.60 (d, J = 5.4 Hz, 1H), 2.53 (dd, J = 17.6, 1.6 Hz, 1H), 2.38 (s, 3H), 1.84 (dq, J = 14.8, 7.5 Hz, 1H), 1.67 (dq, J = 14.6, 7.4, 2.3 Hz, 2H), 1.56 (dq, J = 14.5, 7.1 Hz, 1H), 0.90 (q, J = 7.6 Hz, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 144.64, 143.94,

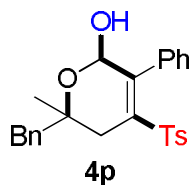
137.54, 137.23, 134.63, 129.27, 128.02, 127.78, 127.66, 92.28, 77.21, 32.43, 28.97, 28.90, 21.55, 8.09, 7.48; HRMS (ESI) m/z : $[M + Na]^+$ Calcd for $C_{22}H_{26}O_4SNa$ 409.1444; Found 409.1449.



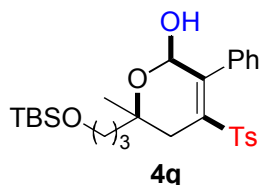
Compound 4n: 58 mg, 78% yield, dr = 1.3:1, colorless oil; Flash column chromatography conditions: petroleum ethers/EtOAc = 3:1; 1H NMR (600 MHz, $CDCl_3$) of major isomer δ 7.30 (dd, J = 16.3, 8.3 Hz, 3H), 7.24 (t, J = 7.2 Hz, 2H), 7.14-7.09 (m, 2H), 7.05-6.86 (m, 2H), 5.43 (d, J = 4.2 Hz, 1H), 2.67 (d, J = 2.9 Hz, 1H), 2.65 (d, J = 9.5 Hz, 1H), 2.52 (dd, J = 25.1, 9.2 Hz, 1H), 2.37 (s, 3H), 1.67 (dd, J = 12.2, 7.4 Hz, 1H), 1.59 (dd, J = 14.4, 7.1 Hz, 1H), 1.38 (s, 3H), 1.15-0.87 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) of major isomer δ 144.64, 143.93, 137.70, 137.23, 134.69, 129.24, 128.04, 127.74, 127.67, 92.47, 74.26, 34.52, 34.05, 24.57, 21.55, 7.79; HRMS (ESI) m/z : $[M + Na]^+$ Calcd for $C_{21}H_{24}O_4SNa$ 395.1288; Found 395.1284.



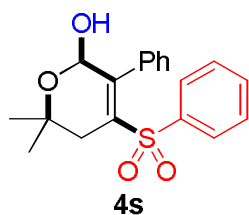
Compound 4o: 50 mg, 60% yield, dr = 3.3:1, colorless oil; Flash column chromatography conditions: petroleum ethers/EtOAc = 3:1; 1H NMR (600 MHz, $CDCl_3$) of major isomer δ 7.39 (d, J = 7.2 Hz, 2H), 7.34 (d, J = 7.2 Hz, 2H), 7.30 (d, J = 7.2 Hz, 1H), 7.27 (d, J = 8.2 Hz, 2H), 7.23 (d, J = 7.4 Hz, 1H), 7.17 (t, J = 7.5 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 6.88-6.60 (m, 2H), 5.25 (d, J = 6.2 Hz, 1H), 3.27 (dd, J = 17.4, 1.4 Hz, 1H), 2.98 (dd, J = 17.4, 1.8 Hz, 1H), 2.85 (d, J = 6.5 Hz, 1H), 2.38 (s, 3H), 1.68 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) of major isomer δ 145.22, 144.04, 137.55, 136.84, 134.21, 129.28, 128.50, 128.01, 127.95, 127.69, 127.59, 125.78, 125.09, 93.17, 75.16, 34.18, 30.69, 21.54; HRMS (ESI) m/z : $[M + Na]^+$ Calcd for $C_{25}H_{24}O_4SNa$ 443.1288; Found 443.1292.



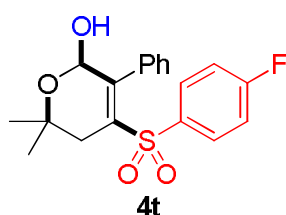
Compound 4p: 57 mg, 66% yield, dr = 1.3:1, colorless oil; Flash column chromatography conditions: petroleum ethers/EtOAc = 3:1; ^1H NMR (600 MHz, CDCl_3) of major isomer δ 7.34 (d, J = 8.2 Hz, 2H), 7.28 (s, 3H), 7.25-7.24 (m, 3H), 7.18 (d, J = 6.9 Hz, 2H), 7.13 (d, J = 8.1 Hz, 2H), 7.08-6.90 (m, 2H), 5.49 (d, J = 4.6 Hz, 1H), 2.93 (d, J = 3.9 Hz, 1H), 2.68-2.64 (m, 2H), 2.62-2.57 (m, 1H), 2.43 (dd, J = 17.5, 1.2 Hz, 1H), 2.37 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3) of major isomer δ 144.46, 143.93, 137.64, 137.18, 136.96, 134.65, 130.78, 129.23, 128.15, 128.07, 127.94, 127.80, 127.68, 126.62, 92.50, 75.31, 47.94, 34.50, 25.36, 24.77, 21.55; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{26}\text{H}_{26}\text{O}_4\text{SNa}$ 457.1444; Found 457.1444.



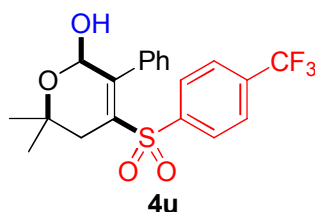
Compound 4q: 56 mg, 54% yield, dr = 1.3:1, colorless oil; Flash column chromatography conditions: petroleum ethers/EtOAc = 3:1; ^1H NMR (600 MHz, CDCl_3) of major isomer δ 7.28 (d, J = 8.2 Hz, 2H), 7.26 (dd, J = 6.3, 2.2 Hz, 1H), 7.21 (td, J = 7.4, 3.5 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 7.04-6.88 (m, 2H), 5.39 (d, J = 4.9 Hz, 1H), 3.61 (d, J = 5.7 Hz, 1H), 3.59-3.51 (m, 1H), 2.98 (d, J = 5.2 Hz, 1H), 2.65 (d, J = 17.6 Hz, 1H), 2.53 (d, J = 17.6 Hz, 1H), 2.36 (s, 3H), 1.71-1.64 (m, 1H), 1.57-1.51 (m, 1H), 1.37 (s, 3H), 0.90 (s, 9H), 0.87 (s, 6H); ^{13}C NMR (151 MHz, CDCl_3) of major isomer δ 144.75, 143.84, 137.45, 137.18, 134.65, 129.18, 127.91, 127.68, 127.54, 92.29, 73.78, 63.16, 37.58, 34.97, 26.72, 25.91, 25.13, 21.48, 18.27, -5.34; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{28}\text{H}_{40}\text{O}_5\text{SSiNa}$ 539.2258; Found 539.2263.



Compound 4s: 48 mg, 70% yield, colorless oil; Flash column chromatography conditions: petroleum ethers/EtOAc = 3:1; ^1H NMR (600 MHz, CDCl_3) δ 7.48 (t, J = 7.4 Hz, 1H), 7.41 (dd, J = 8.3, 1.1 Hz, 2H), 7.35-7.27 (m, 3H), 7.23 (t, J = 7.4 Hz, 2H), 7.10-6.76 (m, 2H), 5.44 (d, J = 4.9 Hz, 1H), 2.76 (d, J = 17.6 Hz, 1H), 2.58 (dd, J = 17.6, 1.5 Hz, 1H), 2.58 (d, J = 5.1 Hz, 1H), 1.45 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 145.01, 140.24, 137.75, 134.38, 132.98, 128.62, 128.15, 127.79, 127.67, 92.61, 72.15, 36.22, 28.43, 27.65; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{19}\text{H}_{20}\text{O}_4\text{SNa}$ 367.0975; Found 367.0971.

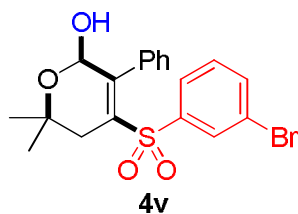


Compound 4t: 46 mg, 63% yield, colorless oil; Flash column chromatography conditions: petroleum ethers/EtOAc = 3:1; ^1H NMR (600 MHz, CDCl_3) δ 7.36 (dd, J = 8.8, 5.1 Hz, 2H), 7.28 (t, J = 7.4 Hz, 1H), 7.22 (t, J = 7.4 Hz, 2H), 7.08-7.02 (m, 1H), 6.94 (t, J = 8.5 Hz, 3H), 5.41 (d, J = 3.7 Hz, 1H), 2.94-2.89 (m, 1H), 2.74 (d, J = 17.7 Hz, 1H), 2.57 (d, J = 17.6 Hz, 1H), 1.44 (s, 3H), 1.37 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 165.22 (d, J = 256.0 Hz), 145.08, 137.85, 136.19, 134.29, 130.44 (d, J = 9.6 Hz), 128.23, 127.79, 115.82 (d, J = 22.7 Hz), 92.45, 72.13, 36.07, 28.37, 27.62; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{19}\text{H}_{19}\text{FO}_4\text{SNa}$ 385.0880; Found 385.0877.

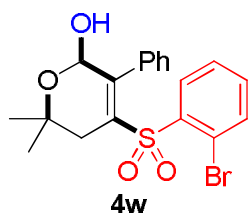


Compound 4u: 50 mg, 61% yield, yellow solid, mp 114-117 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 3:1; ^1H NMR (600 MHz, CDCl_3) δ 7.50 (d, J = 8.3 Hz, 2H), 7.45 (d, J = 8.3 Hz, 2H), 7.25 (tt, J = 7.5, 1.1 Hz, 1H), 7.15 (t, J = 7.3 Hz, 2H), 7.08-6.70 (m, 2H), 5.40 (d, J = 4.9 Hz, 1H), 3.00 (d, J = 5.2 Hz, 1H), 2.78 (dd, J = 17.7, 0.8 Hz, 1H), 2.61 (dd, J = 17.7, 1.7 Hz, 1H), 1.45 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 145.75, 143.73,

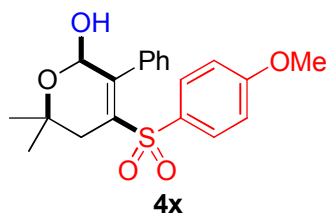
137.73, 134.36 (q, $J = 32.9$ Hz), 133.98, 128.31, 128.10, 127.81, 125.52 (q, $J = 3.6$ Hz), 123.03 (q, $J = 273.0$ Hz), 92.30, 72.15, 35.88, 28.39, 27.59; ^{19}F NMR (565 MHz, CDCl_3) δ -63.27; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{19}\text{F}_3\text{O}_4\text{SNa}$ 435.0848; Found 435.0857.



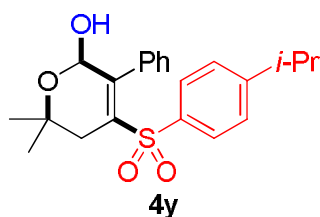
Compound 4v: 58 mg, 69% yield, white solid, mp 122-124 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 3:1; ^1H NMR (600 MHz, CDCl_3) δ 7.57 (d, $J = 7.9$ Hz, 1H), 7.39-7.30 (m, 3H), 7.22 (t, $J = 7.1$ Hz, 2H), 7.18 (t, $J = 7.9$ Hz, 1H), 7.10-6.62 (m, 2H), 5.43 (d, $J = 4.9$ Hz, 1H), 2.88 (d, $J = 5.2$ Hz, 1H), 2.77 (d, $J = 17.7$ Hz, 1H), 2.59 (d, $J = 17.6$ Hz, 1H), 1.46 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 145.67, 142.07, 137.78, 136.00, 133.78, 130.78, 130.04, 128.55, 127.79, 126.02, 122.53, 92.40, 72.17, 36.01, 28.42, 27.61; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{19}\text{H}_{19}\text{BrO}_4\text{SNa}$ 445.0080; Found 445.0074.



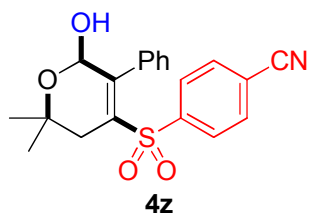
Compound 4w: 57 mg, 68% yield, white solid, mp 143-144 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 3:1; ^1H NMR (600 MHz, CDCl_3) δ 7.52 (d, $J = 7.9$ Hz, 1H), 7.23 (dd, $J = 7.9, 1.3$ Hz, 1H), 7.17 (td, $J = 7.8, 1.5$ Hz, 1H), 7.07 (t, $J = 7.4$ Hz, 1H), 7.03-6.96 (m, 1H), 6.94 (t, $J = 7.7$ Hz, 1H), 5.49 (d, $J = 5.0$ Hz, 1H), 2.86 (d, $J = 18.0$ Hz, 1H), 2.83 (d, $J = 5.1$ Hz, 1H), 2.78 (d, $J = 17.9$ Hz, 1H), 1.54 (s, 3H), 1.46 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 143.83, 139.65, 137.37, 134.15, 133.63, 133.44, 131.23, 128.16, 127.57, 127.25, 120.15, 92.26, 72.33, 35.33, 28.85, 27.89; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{19}\text{H}_{19}\text{BrO}_4\text{SNa}$ 445.0080; Found 445.0077.



Compound 4x: 30 mg, 40% yield, white solid, mp 108-109 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 3:1; ^1H NMR (600 MHz, CDCl_3) δ 7.34 (d, J = 8.8 Hz, 2H), 7.31-7.23 (m, 3H), 7.12-6.92 (m, 2H), 6.77 (d, J = 8.8 Hz, 3H), 5.43 (d, J = 3.2 Hz, 1H), 3.83 (s, 3H), 2.72 (d, J = 5.1 Hz, 1H), 2.72 (d, J = 17.5 Hz, 1H), 2.57 (s, 1H), 1.44 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 163.21, 144.16, 137.97, 134.65, 131.65, 129.92, 128.08, 127.74, 113.87, 92.62, 72.11, 55.60, 36.21, 28.34, 27.66; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{22}\text{O}_5\text{SNa}$ 397.1080; Found 397.1083.

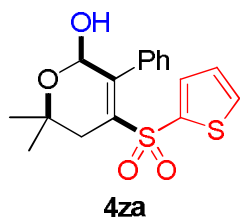


Compound 4y: 46 mg, 60% yield, colorless oil; Flash column chromatography conditions: petroleum ethers/EtOAc = 3:1; ^1H NMR (600 MHz, CDCl_3) δ 7.30 (d, J = 8.3 Hz, 2H), 7.28-7.23 (m, 1H), 7.19 (t, J = 7.5 Hz, 2H), 7.12 (d, J = 8.4 Hz, 2H), 7.05-6.83 (m, 2H), 5.40 (d, J = 4.4 Hz, 1H), 2.91 (m, 2H), 2.74 (d, J = 17.6 Hz, 1H), 2.57 (d, J = 17.6 Hz, 1H), 1.43 (s, 3H), 1.36 (s, 3H), 1.23 (d, J = 6.9 Hz, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 154.53, 144.45, 137.89, 137.40, 134.48, 127.94, 127.79, 127.65, 126.66, 92.50, 72.13, 36.05, 34.12, 28.29, 27.64, 23.60, 23.54; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{22}\text{H}_{26}\text{O}_4\text{SNa}$ 409.1444; Found 409.1441.



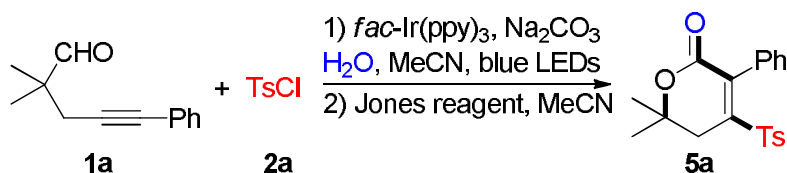
Compound 4z: 43 mg, 58% yield, white solid, mp 144-145 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 3:1; ^1H NMR (600 MHz, CDCl_3) δ 7.54 (d, J = 8.4 Hz, 2H),

7.43 (d, $J = 8.4$ Hz, 2H), 7.29 (t, $J = 7.5$ Hz, 1H), 7.20 (t, $J = 7.2$ Hz, 2H), 7.11-6.61 (m, 2H), 5.44 (d, $J = 4.9$ Hz, 1H), 2.80 (d, $J = 17.8$ Hz, 1H), 2.76 (d, $J = 5.1$ Hz, 1H), 2.62 (dd, $J = 17.8, 1.5$ Hz, 1H), 1.47 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 146.16, 144.51, 137.67, 133.89, 132.14, 128.52, 128.17, 127.93, 117.14, 116.38, 92.33, 72.16, 35.95, 28.54, 27.61; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{19}\text{NO}_4\text{SNa}$ 392.0927; Found 392.0927.



Compound 4za: 47 mg, 67% yield, yellow oil; Flash column chromatography conditions: petroleum ethers/EtOAc = 3:1; ^1H NMR (600 MHz, CDCl_3) δ 7.59 (d, $J = 4.8$ Hz, 1H), 7.32 (q, $J = 5.9$ Hz, 3H), 7.15 (d, $J = 3.3$ Hz, 1H), 7.12 (s, 2H), 6.94-6.91 (m, 1H), 5.48 (d, $J = 4.9$ Hz, 1H), 2.73 (d, $J = 17.5$ Hz, 1H), 2.61 (d, $J = 9.1$ Hz, 1H), 2.59 (d, $J = 17.6$ Hz, 1H), 1.44 (s, 3H), 1.37 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 145.11, 141.02, 137.47, 134.55, 134.37, 133.89, 128.25, 127.84, 127.31, 92.70, 72.14, 36.10, 28.31, 27.62; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{17}\text{H}_{18}\text{O}_4\text{S}_2\text{Na}$ 373.0539; Found 373.0546.

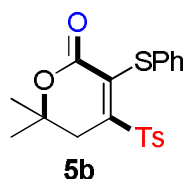
General Procedure for the One-Pot Synthesis of Dihydropyranones **5**



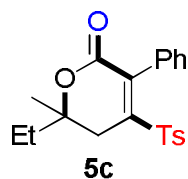
To a mixture of *fac*-Ir(ppy)₃ (2.6 mg, 0.004 mmol), Na₂CO₃ (42.4 mg, 0.4 mmol), H₂O (7.2 μL , 0.4 mmol) and **2a** (57.0 mg, 0.3 mmol) in 2 mL of dry MeCN was added **1a** (37.2 mg, 0.2 mmol) under a nitrogen atmosphere. After 5 h of irradiation at a distance of ~5 cm from 15 W blue LEDs (BESTLLON[®] lamps, 450 nm, 100% light intensity) at 50 °C, Jones reagent (1.7 M solution of CrO₃ in aq H₂SO₄) (0.24 mL, 0.4 mmol) was added at 25 °C. After stirring at room temperature for 5 h, the reaction mixture was concentrated and purified by column chromatography on silica gel (petroleum ethers/EtOAc = 3:1) to give 57 mg (80% yield) of **5a** as a white solid; mp

159-160 °C; ^1H NMR (600 MHz, CDCl_3) δ 7.31 (t, J = 7.5 Hz, 1H), 7.22 (dd, J = 15.6, 7.9 Hz, 4H), 7.08 (d, J = 8.0 Hz, 2H), 6.99 (d, J = 7.3 Hz, 2H), 3.04 (s, 2H), 2.36 (s, 3H), 1.55 (s, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 163.30, 149.58, 144.97, 135.63, 135.50, 130.99, 129.88, 129.50, 128.87, 128.07, 127.57, 79.90, 36.28, 27.21, 21.64; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{20}\text{O}_4\text{SNa}$ 379.0975; Found 379.0982.

Crystal data for **5a** ($\text{C}_{20}\text{H}_{20}\text{O}_4\text{S}$, 356.45): orthorhombic, space group $P2_12_12_1$, a = 10.8083(4) Å, b = 11.6866(6) Å, c = 14.3467(6) Å, V = 1812.16(14) Å³, Z = 4, T = 250.0 K, μ = 0.200 mm⁻¹, reflections collected 15036, independent reflections 4091 [R_{int} = 0.0244], refinement by full-matrix least-squares on F^2 , data/restraints/parameters 4091/0/228, goodness-of-fit on F^2 = 1.153, final R indices [$I > 2s(I)$] R_1 = 0.0311, wR_2 = 0.0874, R indices (all data) R_1 = 0.0374, wR_2 = 0.0979, largest diff peak and hole 0.28 and -0.37 e.Å⁻³. Crystallographic data for the structure of **5a** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 2060838.

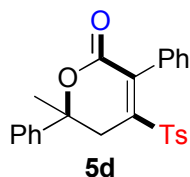


Compound 5b: 46 mg, 59% yield, yellow solid, mp 126-128 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 3:1; ^1H NMR (600 MHz, CDCl_3) δ 7.99 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 8.1 Hz, 2H), 7.23-7.16 (m, 3H), 7.01 (d, J = 6.9 Hz, 2H), 3.03 (s, 2H), 2.46 (s, 3H), 1.36 (s, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 158.91, 150.46, 145.95, 135.67, 135.08, 132.50, 131.88, 129.86, 129.06, 128.71, 128.26, 79.37, 38.21, 26.85, 21.74; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{20}\text{O}_4\text{S}_2\text{Na}$ 411.0695; Found 411.0703.

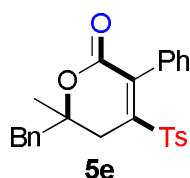


Compound 5c: 56 mg, 76% yield, white solid, mp 148-149 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 3:1; ^1H NMR (600 MHz, CDCl_3) δ 7.31 (t, J = 7.5 Hz, 2H),

7.25-7.19 (m, 4H), 7.08 (d, $J = 8.1$ Hz, 2H), 6.98 (d, $J = 7.0$ Hz, 2H), 3.02 (dd, $J = 45.9, 18.4$ Hz, 2H), 2.36 (s, 3H), 1.86 (ddt, $J = 21.7, 14.2, 7.3$ Hz, 2H), 1.50 (s, 3H), 1.03 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 163.26, 149.47, 144.87, 135.58, 135.42, 130.97, 129.80, 129.42, 128.78, 128.00, 127.50, 82.33, 33.99, 32.98, 24.14, 21.57, 8.11; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{21}\text{H}_{22}\text{O}_4\text{SNa}$ 393.1131; Found 393.1139.

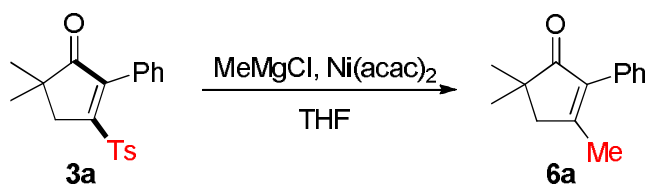


Compound 5d: 53 mg, 63% yield, colorless oil; Flash column chromatography conditions: petroleum ethers/EtOAc = 3:1; ^1H NMR (600 MHz, CDCl_3) δ 7.41-7.32 (m, 5H), 7.23 (t, $J = 7.5$ Hz, 1H), 7.10 (t, $J = 7.3$ Hz, 2H), 6.95 (q, $J = 8.3$ Hz, 4H), 6.66 (s, 2H), 3.80 (d, $J = 18.0$ Hz, 1H), 3.26 (d, $J = 18.0$ Hz, 1H), 2.33 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 163.86, 149.09, 144.64, 142.08, 136.83, 135.27, 130.84, 129.24, 128.84, 128.69, 128.00, 127.94, 127.44, 124.63, 83.37, 35.72, 30.29, 21.54; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{25}\text{H}_{22}\text{O}_4\text{SNa}$ 441.1131; Found 441.1138.



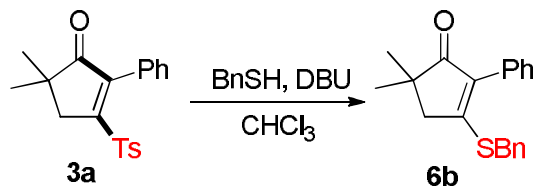
Compound 5e: 54 mg, 63% yield, white solid, mp 159-160 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 3:1; ^1H NMR (600 MHz, CDCl_3) δ 7.36 (t, $J = 7.2$ Hz, 2H), 7.33-7.30 (m, 2H), 7.28 (d, $J = 8.2$ Hz, 2H), 7.22-7.18 (m, 4H), 7.05 (d, $J = 8.1$ Hz, 2H), 6.94 (d, $J = 7.5$ Hz, 2H), 3.19 (d, $J = 13.8$ Hz, 1H), 3.12 (d, $J = 18.6$ Hz, 1H), 3.07 (d, $J = 13.8$ Hz, 1H), 2.95 (d, $J = 18.6$ Hz, 1H), 2.37 (s, 3H), 1.53 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 163.03, 149.69, 144.86, 135.54, 134.84, 130.71, 129.91, 129.40, 128.84, 128.64, 128.05, 127.53, 127.32, 81.92, 46.23, 33.78, 25.50, 21.62; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{26}\text{H}_{24}\text{O}_4\text{SNa}$ 455.1288; Found 455.1294.

Experimental Procedure for the Synthesis of **6a**²



To a mixture of **3a** (68.0 mg, 0.2 mmol) and Ni(acac)₂ (5.1 mg, 0.02 mmol) in 1 mL of THF was slowly added 1.0 M MeMgCl (0.24 mL, 0.24 mmol) at 0 °C. After stirring at room temperature for 10 h, the reaction mixture is quenched with saturated NH₄Cl solution and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, and concentrated. Column chromatography on silica gel (petroleum ethers/EtOAc = 8:1) gave 22 mg (54% yield) of **6a** as a colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 7.43-7.38 (m, 2H), 7.33-7.29 (m, 3H), 2.53 (d, *J* = 0.8 Hz, 2H), 2.17 (s, 3H), 1.19 (s, 6H); ¹³C NMR (151 MHz, CDCl₃) δ 211.71, 168.34, 137.38, 132.04, 129.16, 128.15, 127.47, 48.92, 43.27, 25.24, 18.18; HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₁₄H₁₆ONa 223.1093; Found 223.1096.

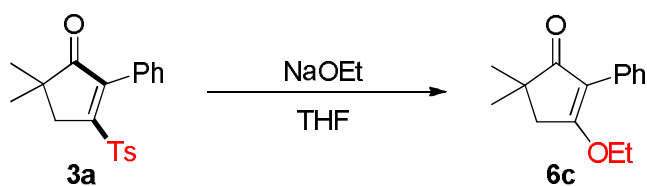
Experimental Procedure for the Synthesis of **6b**



To a solution of **3a** (68.0 mg, 0.2 mmol) and DBU (60.8 mg, 0.4 mmol) in 2 mL of CHCl₃ was added BnSH (49.6 mg, 0.4 mmol) at 0 °C. After stirring at 25 °C for 10 h, the reaction mixture was concentrated and purified by column chromatography on silica gel (petroleum ethers/EtOAc = 5:1) to give 53 mg (86% yield) of **6b** as a colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 7.50 (d, *J* = 7.2 Hz, 2H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.33 (d, *J* = 4.3 Hz, 4H), 7.28 (dt, *J* = 7.4, 2.7 Hz, 2H), 4.18 (s, 2H), 2.82 (s, 2H), 1.20 (s, 6H); ¹³C NMR (151 MHz, CDCl₃) δ 207.22, 168.85, 135.60, 133.44, 131.62, 128.92, 128.91, 128.84, 128.16, 127.88, 127.80, 46.31, 43.94, 35.31, 25.43; HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₂₀H₂₀OSNa 331.1127; Found 331.1130.

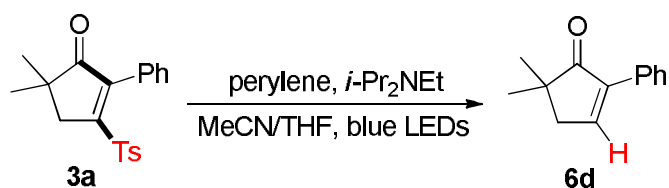
Experimental Procedure for the Synthesis of **6c**

² J. L. Fabre, M. Julia and J. N. Verpeaux, *Tetrahedron Lett.*, 1982, **23**, 2469.



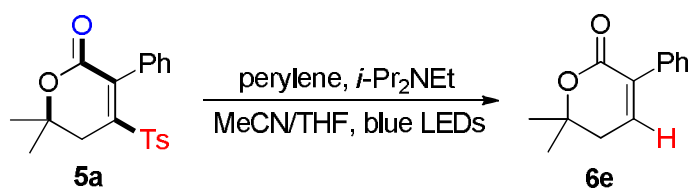
To a solution of **3a** (68.0 mg, 0.2 mmol) in 2 mL of dry THF₃ was added NaOEt (27.2 mg, 0.4 mmol) at 0 °C. After stirring at 25 °C for 10 h, the reaction mixture was concentrated and purified by column chromatography on silica gel (petroleum ethers/EtOAc = 5:1) to give 46 mg (99% yield) of **6c** as a colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 7.81 (dd, *J* = 8.2, 1.1 Hz, 2H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.23 (t, *J* = 7.4 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.66 (s, 2H), 1.44 (t, *J* = 7.1 Hz, 3H), 1.23 (s, 6H); ¹³C NMR (151 MHz, CDCl₃) δ 207.91, 181.50, 131.12, 128.08, 127.82, 126.67, 114.93, 65.75, 43.08, 41.28, 25.51, 15.16; HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₁₅H₁₈NaO₂ 253.1199; Found 253.1205.

Experimental Procedure for the Synthesis of **6d**



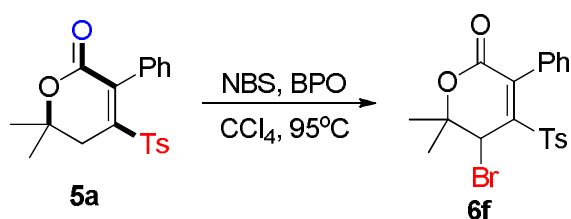
To a solution of **3a** (68.1 mg, 0.2 mmol) and perylene (2.6 mg, 0.01 mmol) in 2 mL of 5:1 mixture of acetonitrile and THF was added *i*-Pr₂NEt (81.0 mg, 1.6 mmol) under a nitrogen atmosphere.³ After 10 h of irradiation at a distance of ~5 cm from 15 W blue LEDs (BESTLLON[®] lamps, 450 nm, 100% light intensity) at 25 °C, the reaction mixture was concentrated and purified by column chromatography on silica gel (petroleum ethers/EtOAc = 20:1) to give 30 mg (81% yield) of **6d** as a white solid; mp 39-40 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.73 (d, *J* = 7.7 Hz, 3H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 1H), 2.58 (s, 2H), 1.20 (s, 6H); ¹³C NMR (151 MHz, CDCl₃) δ 211.86, 155.67, 140.63, 131.97, 128.37, 128.27, 127.02, 44.37, 43.21, 25.25; HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₁₃H₁₅O 187.1117; Found 187.1134.

³ H. Watanabe, M. Takemoto, K. Adachi, Y. Okuda, A. Dakegata, T. Fukuyama, I. Ryu, K. Wakamatsu and A. Orita, *Chem. Lett.*, 2020, **49**, 409.



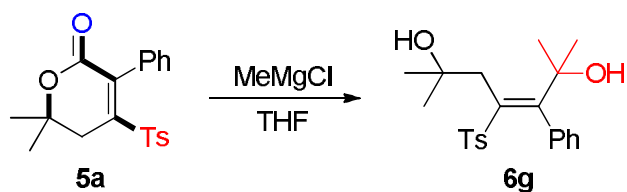
Compound 6e: 34 mg, 84% yield, yellow solid; mp 55-56 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 10:1; ^1H NMR (600 MHz, CDCl_3) δ 7.46 (d, J = 7.1 Hz, 2H), 7.37 (t, J = 7.3 Hz, 2H), 7.33 (t, J = 7.2 Hz, 1H), 6.84 (t, J = 4.6 Hz, 1H), 2.61 (d, J = 4.6 Hz, 2H), 1.53 (s, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 163.75, 139.42, 135.62, 132.83, 128.29, 128.22, 128.18, 80.09, 36.38, 27.74; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{13}\text{H}_{14}\text{O}_2\text{Na}$ 225.0886; Found 225.0886.

Experimental Procedure for the Synthesis of 6f



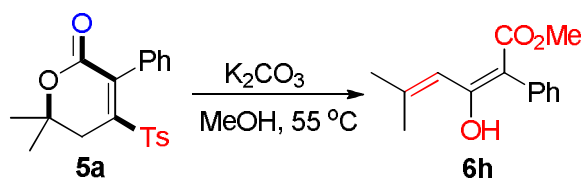
To a solution of **5a** (71.2 mg, 0.2 mmol) and BPO (9.7 mg, 0.04 mmol) in 1 mL of CCl_4 was added NBS (106.8 mg, 0.6 mmol) under a nitrogen atmosphere. After stirring at 95 °C for 10 h, the reaction mixture was concentrated and purified by column chromatography on silica gel (petroleum ethers/EtOAc = 3:1) to give 56 mg (65% yield) of **6f** as a white solid; mp 149-150 °C; ^1H NMR (600 MHz, CDCl_3) δ 7.33 (t, J = 7.5 Hz, 1H), 7.21 (dd, J = 12.6, 7.9 Hz, 4H), 7.03 (d, J = 8.1 Hz, 2H), 6.93 (d, J = 6.6 Hz, 2H), 5.44 (s, 1H), 2.36 (s, 3H), 1.78 (d, J = 20.4 Hz, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 161.73, 152.18, 145.12, 136.80, 135.11, 129.77, 129.60, 129.28, 128.42, 127.57, 80.93, 47.14, 28.40, 24.93, 21.66; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{19}\text{BrO}_4\text{SNa}$ 457.0080; Found 457.0072.

Experimental Procedure for the Synthesis of 6g



To a solution of **5a** (71.2 mg, 0.2 mmol) in 2 mL of THF was added MeMgCl (0.20 mL, 0.6 mmol, 3.0 M solution in THF) at 0 °C under a nitrogen atmosphere. After stirring at room temperature for 10 h, the reaction mixture is quenched with saturated NH₄Cl solution, and extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄ and concentrated. Column chromatography on silica gel (petroleum ethers/EtOAc = 2:1) gave 64 mg (82% yield) of **6g** as a white solid; mp 163-164 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.22-6.62 (m, 9H), 3.71 (s, 2H), 2.36 (s, 3H), 1.54 (s, 6H), 1.16 (s, 6H); ¹³C NMR (151 MHz, CDCl₃) δ 161.57, 146.05, 142.52, 140.84, 139.55, 137.07, 128.96, 127.00, 126.56, 126.36, 75.91, 71.68, 38.68, 31.07, 21.49; HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₂₂H₂₈O₄SNa 411.1601; Found 411.1606.

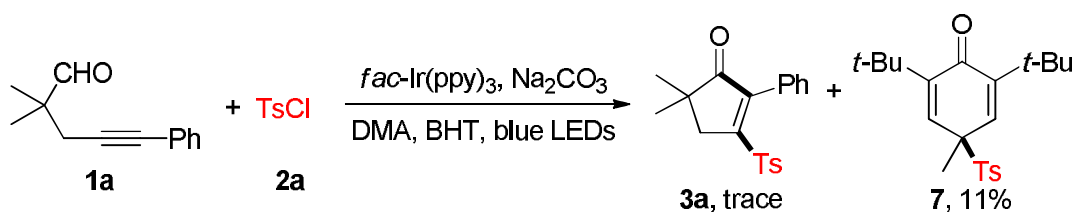
Experimental Procedure for the Synthesis of **6h**



To a solution of **5a** (71.2 mg, 0.2 mmol) in 2 mL of MeOH was added K₂CO₃ (110.6 mg, 0.8 mmol). After stirring at 55 °C for 10 h, the reaction mixture was concentrated. Column chromatography on silica gel (DCM/MeOH = 40:1) gave 44 mg (95% yield) of **6h** as a yellow oil; ¹H NMR (600 MHz, CDCl₃) δ 7.35 (t, *J* = 7.5 Hz, 2H), 7.28-7.24 (m, 3H), 6.06 (s, 1H), 3.50 (s, 3H), 1.89 (s, 3H), 1.79 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 173.41, 165.87, 142.97, 135.86, 130.38, 127.89, 126.85, 118.07, 113.69, 56.77, 25.91, 20.08; HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₁₄H₁₆O₃SNa 255.0992; Found 255.0991.

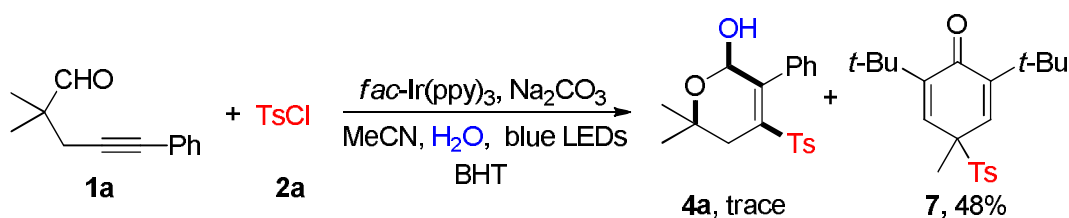
Mechanistic Experiments

Effect of BHT on the Synthesis of **3a** and **4a**



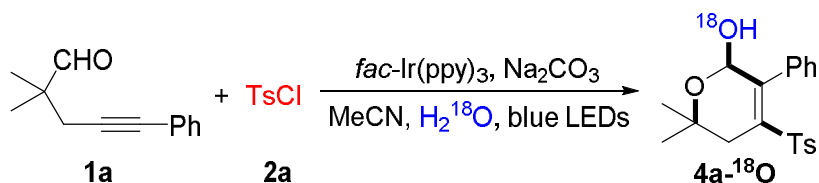
To a mixture of *fac*-Ir(ppy)₃ (2.6 mg, 0.004 mmol), Na₂CO₃ (42.4 mg, 0.4 mmol), H₂O (7.2 μL,

0.4 mmol), and **2a** (57.0 mg, 0.3 mmol) in 2 mL of DMA was added **1a** (37.2 mg, 0.2 mmol) and BTH (88.0 mg, 0.4 mmol) under a nitrogen atmosphere. After 5 h of irradiation at a distance of ~5 cm from 15 W blue LEDs (BESTLLON® lamps, 450 nm, 100% light intensity) at 25 °C, the reaction mixture was concentrated and column chromatography on silica gel (petroleum ethers/EtOAc = 20:1) gave 12 mg (11% yield) of **7** as a white solid; mp 76-77 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.51 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.63 (s, 2H), 2.36 (s, 3H), 1.81 (s, 4H), 1.09 (s, 18H); ¹³C NMR (151 MHz, CDCl₃) δ 183.65, 151.17, 145.26, 135.67, 130.57, 130.22, 128.76, 65.78, 35.16, 28.95, 21.59, 18.50; HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₂₂H₃₀O₃SNa 397.1808; Found 397.1815.



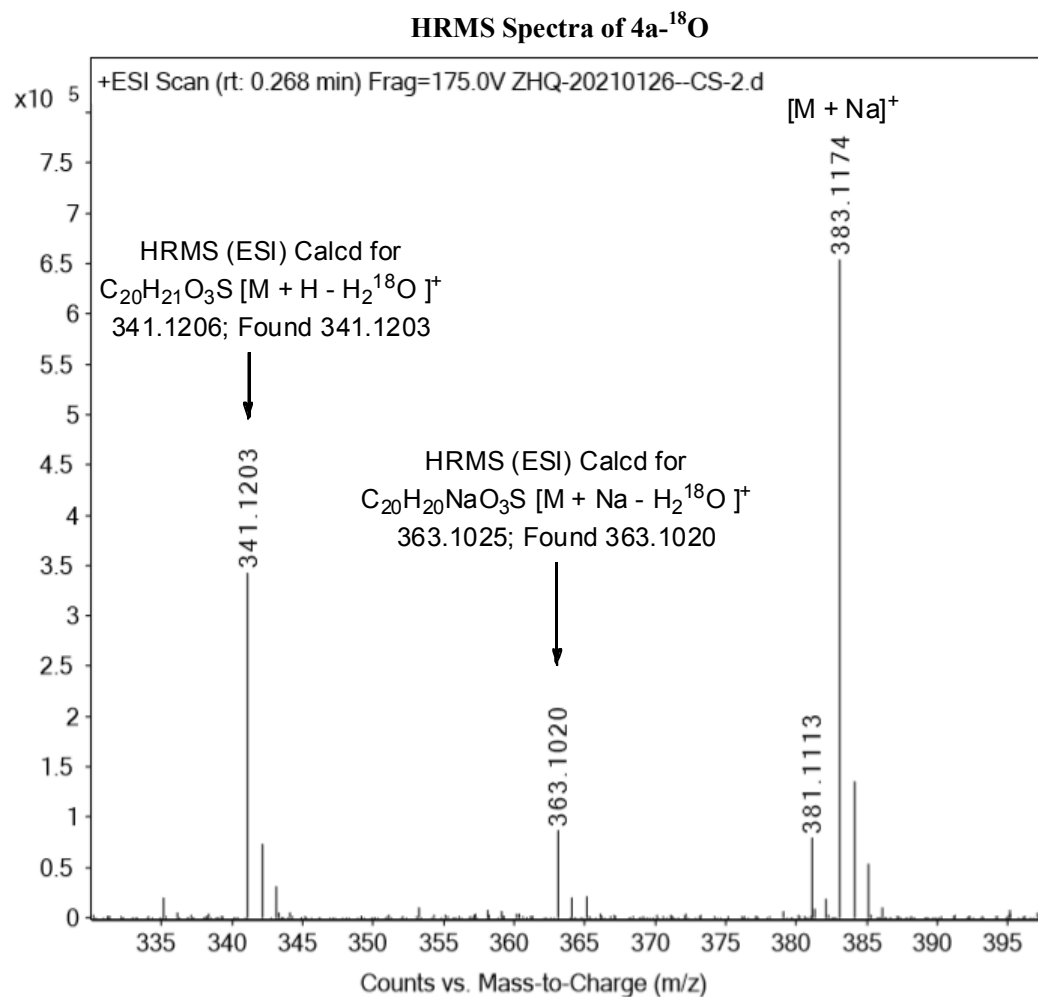
To a mixture of *fac*-Ir(ppy)₃ (2.6 mg, 0.004 mmol), Na₂CO₃ (42.4 mg, 0.4 mmol), H₂O (7.2 μL, 0.4 mmol), and **2a** (57.0 mg, 0.3 mmol) in 2 mL of dry MeCN was added **1a** (37.2 mg, 0.2 mmol) and BTH (88.0 mg, 0.4 mmol) under a nitrogen atmosphere. After 5 h of irradiation at a distance of ~5 cm from 15 W blue LEDs (BESTLLON® lamps, 450 nm, 100% light intensity) at 50 °C, the reaction mixture was concentrated and column chromatography on silica gel (petroleum ethers/EtOAc = 20:1) gave 54 mg (48% yield) of **7** as a white solid.

ESI-HRMS Analysis of the ¹⁸O-Labeled Compounds



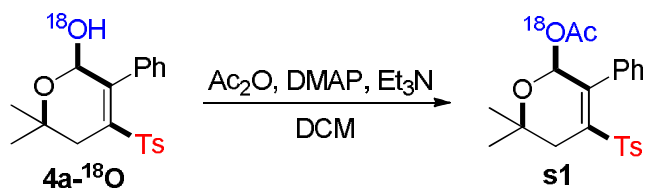
To a mixture of *fac*-Ir(ppy)₃ (2.6 mg, 0.004 mmol), Na₂CO₃ (42.4 mg, 0.4 mmol), H₂¹⁸O (20 μL, 1.0 mmol) and **2a** (57.0 mg, 0.3 mmol) in 2 mL of dry MeCN was added **1a** (37.2 mg, 0.2 mmol) under a nitrogen atmosphere. After 5 h of irradiation at a distance of ~5 cm from 15 W blue LEDs (BESTLLON® lamps, 450 nm, 100% light intensity) at 50 °C, the reaction mixture was concentrated. Column chromatography on silica gel (petroleum ethers/EtOAc = 3:1) gave 50 mg (69% yield) of **4a-¹⁸O** (89% ¹⁸O) as a colorless oil; HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for

$C_{20}H_{22}O_3^{18}OSNa$ 383.1173; Found 383.1174. Observation of the signals of 341.1203 and 363.1020, matched with the $[M + H - H_2^{18}O]^+$ and $[M + Na - H_2^{18}O]^+$ ion, respectively, indicated that the hydroxy group of **4a** is originated from water.



Peak List

m/z	z	Abund
341.121	1	590930.5
342.124	1	129169.52
363.1029		290051.72
423.1235		108912.09
425.1284	1	718021.63
426.131	1	173284.36
825.2624	1	160379.17
827.2676		544489.56
828.2706	1	261463.83
829.2694	1	129009.34

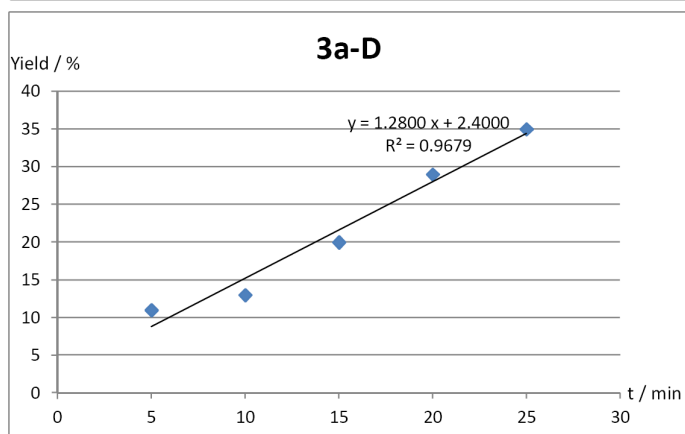
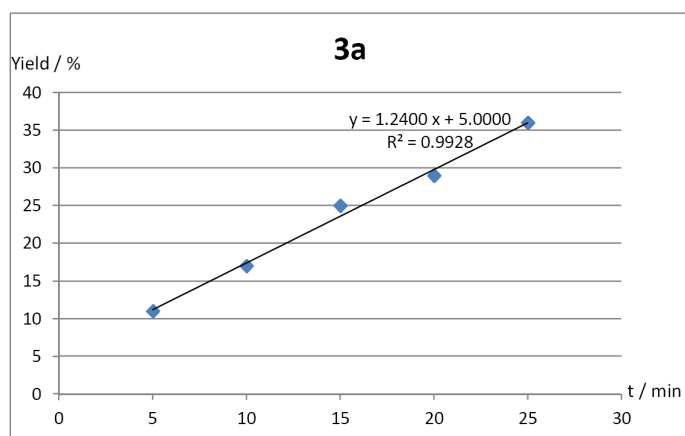


To a solution of **4a-¹⁸O** (89% ¹⁸O, 76.6 mg, 0.2 mmol), Et₃N (55.6 μL, 0.4 mmol), and DMAP (0.5 mg, 0.004 mmol) in 2 mL of dry DCM was added Ac₂O (37.8 μL, 0.4 mmol) under a nitrogen atmosphere. After stirring at room temperature for 10 h, the reaction mixture was concentrated and column chromatography on silica gel (petroleum ethers/EtOAc = 5:1) gave 72 mg (90% yield) of **s1** (87% ¹⁸O) as a white solid; mp 163-164 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.29 (d, *J* = 8.3 Hz, 2H), 7.26 (t, *J* = 7.4 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 2H), 7.05-6.85 (m, 2H), 6.44 (d, *J* = 1.6 Hz, 1H), 2.78 (d, *J* = 17.8 Hz, 1H), 2.54 (dd, *J* = 17.8, 1.5 Hz, 1H), 2.36 (s, 3H), 1.79 (s, 3H), 1.39 (s, 3H), 1.39 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 169.30, 144.09, 142.39, 138.93, 136.89, 133.43, 129.26, 128.22, 127.74, 127.59, 90.61, 72.54, 35.96, 29.45, 26.15, 21.50, 20.64; HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₂₂H₂₄O₄¹⁸OSNa 425.1279; Found 425.1284. Observation of the signals of 341.1210 and 363.1029, matched with the [M + H - H¹⁸OAc]⁺ and [M + Na - H¹⁸OAc]⁺ ion, respectively, further confirmed that the hydroxy group of **4a** is originated from water.

HRMS Spectra of **s1**

The parallel intermolecular KIE experiments were conducted with **1a** (0.1 mmol) and **1a-D** (>98% D, 0.1 mmol) respectively in 3 mL of DMA and H₂O (2.0 equiv) using the general procedure. Reaction progress was monitored by GC. Rate constants were determined by adding the corresponding products with naphthalene as internal standard over time and extracting the slope after linear fitting of the data (simulating the linear function and slope as the rate constants).

t/min	yield of 3a	yield of 3a-D
5	11	11
10	17	13
15	25	20
20	29	29
25	36	35



$$\text{KIE} = k_{\text{H}}/k_{\text{D}} = 1.24/1.28 = 1.0$$

Computational details: All density functional theory (DFT) calculations were performed using

Gaussian 16.⁴ Geometry optimizations and frequencies were calculated at the B3LYP-D3(BJ)/6-31G(d,p)-SDD(Ir) level of theory.^{5,6} Frequency calculations confirmed that optimized structures are minima (no imaginary frequency) or transition structures (one imaginary frequency). To obtain more accurate electronic energies, single-point energy calculations were performed at the ωb97xd/def2tzvpp-SMD level of theory with the optimized structures.⁷ Structures were generated using CYLview.⁸ Grimme's quasi-RRHO correction⁹ for the frequencies that are below 100 cm⁻¹ and was implemented by the GoodVibes.¹⁰ Concentrations for MeCN and DMA are corrected from 1 atm to 19.0 and 10.8 mol/L respectively (the solvent concentrations), concentrations for other species are corrected from 1 atm to 1 mol/L.

⁴ M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, Jr. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, *Gaussian 16, Revision A.03*, Gaussian, Inc., Wallingford CT, 2016.

⁵ (a) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1988, **37**, 785. (b) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.

⁶ D. Andrae, U. Häußermann, M. Dolg, H. Stoll and H. Preuß, *Theoretica Chimica Acta*, 1990, **77**, 123.

⁷ A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2009, **113**, 6378.

⁸ C. Y. Legault, CYLview, 1.0b; Université de Sherbrooke, Sherbrooke, Canada, 2009; <http://www.cylview.org>.

⁹ S. Grimme, *Chem. Eur. J.*, 2012, **18**, 9955.

¹⁰ G. Luchini, J. Alegre-Requena, IFunes, J. Rodríguez-Guerra, J. Chen and R. Paton, 2019, GoodVibes: GoodVibes 3.0.0 <http://doi.org/10.5281/zenodo.595246>.

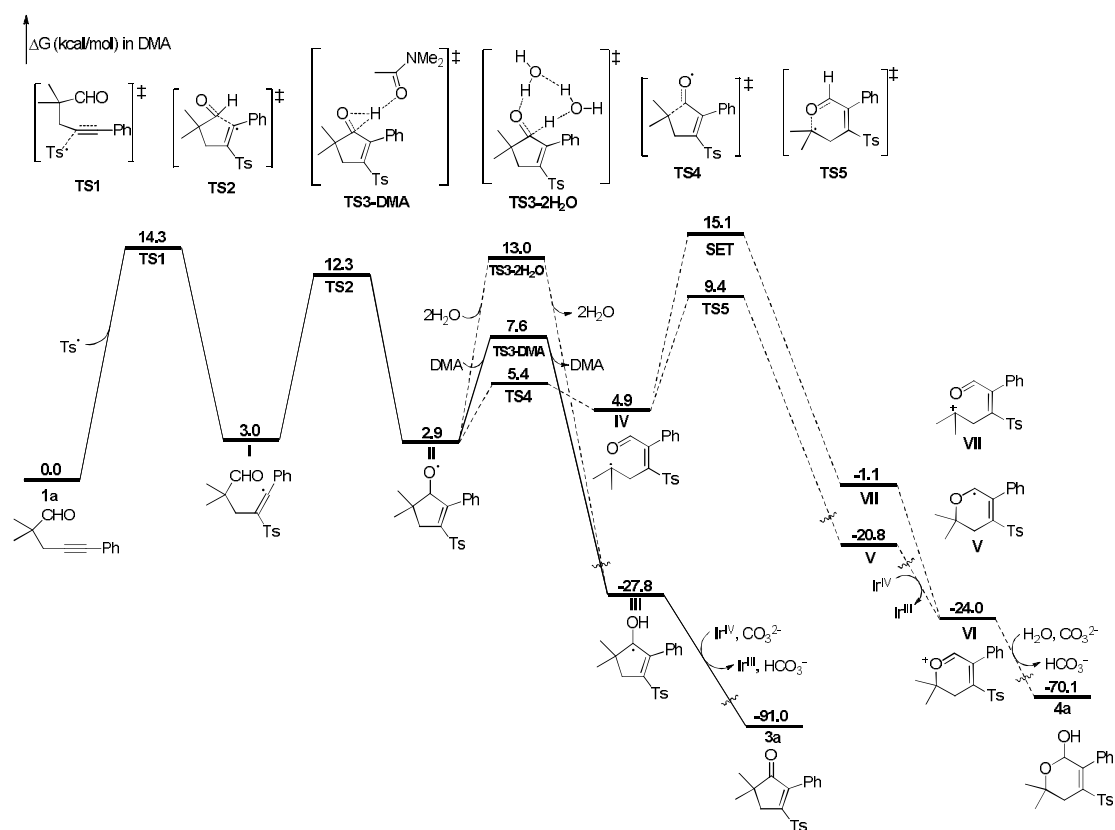


Figure S1. The calculated relative Gibbs free energies for the intermediates and transition-states of the model reaction in DMA at the ω b97xd/def2tzvp-SMD//B3LYP-D3(BJ)/6-31G(d,p) level of theory.

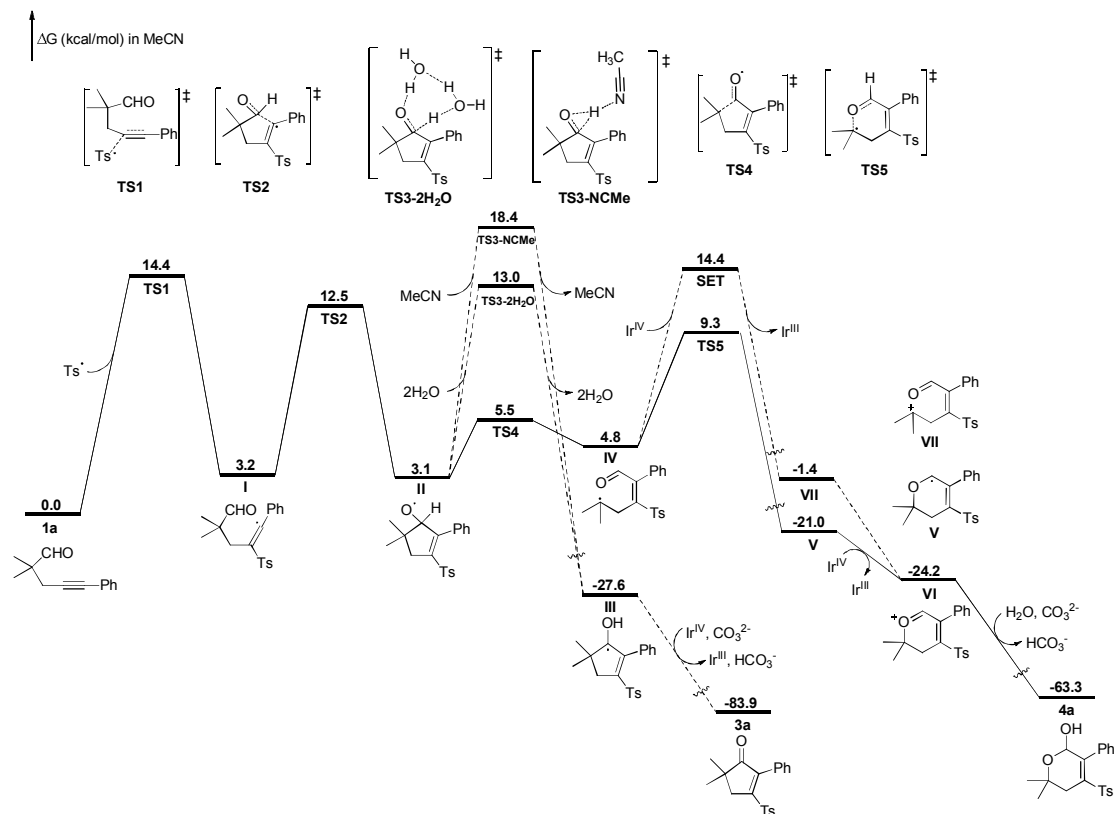


Figure S2. The calculated relative Gibbs free energies for the intermediates and transition-states

of the model reaction in MeCN at the ω b97xd/def2tzvp-SMD//B3LYP-D3(BJ)/6-31G(d,p) level of theory.

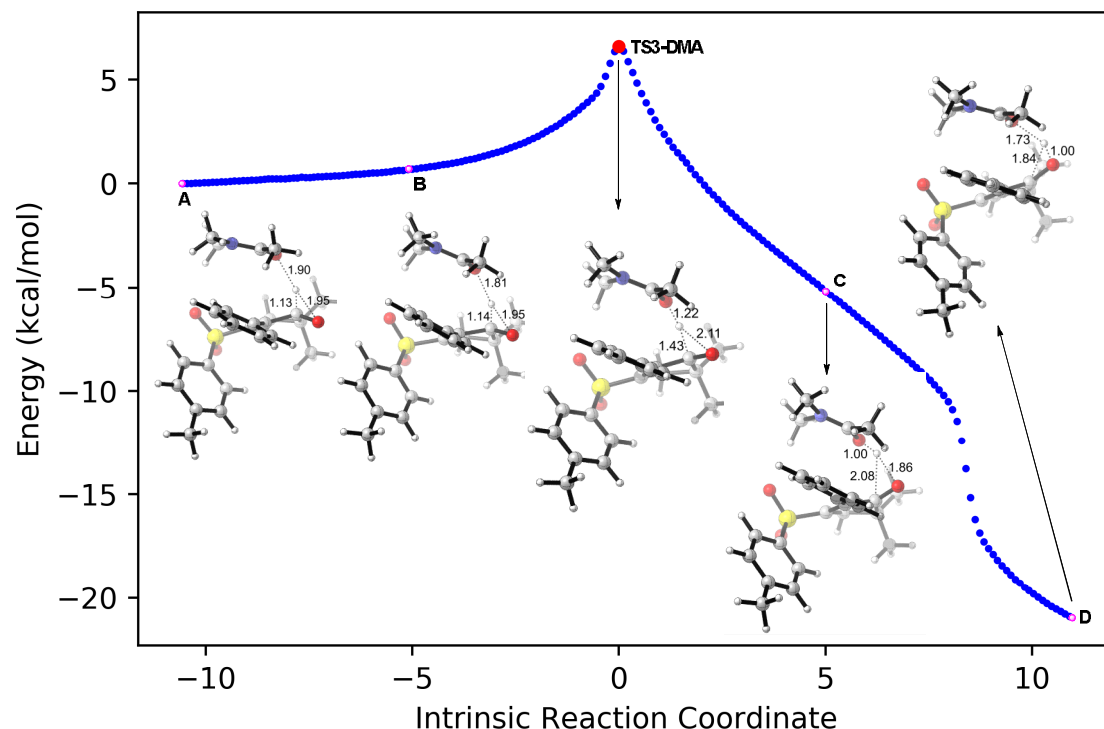


Figure S3. The intrinsic reaction coordinate for TS3-DMA.

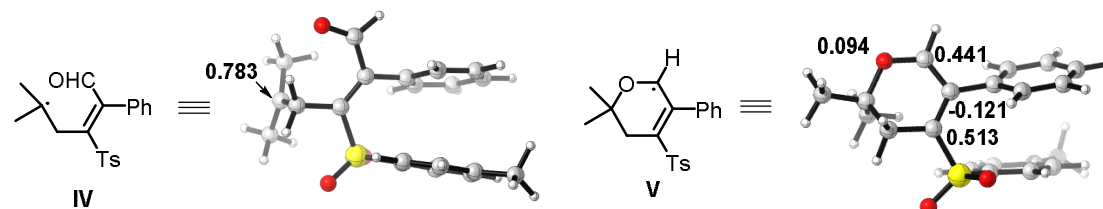


Figure S4. The Mulliken spin distribution of intermediate IV and V in MeCN.

Calculation details of the barrier of single electron transfer process between intermediate IV and *fac*-Ir^{IV}(ppy)₃ process using Marcus-Hush theory.

According to the Marcus-Hush theory of electron transfer, the free energy barrier of a single electron transfer process can be estimated from the outer-sphere electron transfer model:

$$\Delta G_{SET}^{\ddagger} = \frac{(\Delta G_r + \lambda)^2}{4\lambda}$$

where ΔG_r is the free energy change of the electron transfer reaction, and λ is the total reorganization energy, which can be estimated as the sum of the internal reorganization energy (λ_i) and external reorganization energy (λ_e). For an electron transfer reaction, the internal reorganization energy λ_i can be neglected, and so the total reorganization energy $\lambda \approx \lambda_e$. The external reorganization energy can be calculated according to:

$$\lambda_e = (332 \text{ kcal/mol}) \left(\frac{1}{a_1} + \frac{1}{a_2} - \frac{1}{a_1 + a_2} \right) \left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon} \right)$$

where a_1 and a_2 are the radii of the reactants, ϵ_{op} is the optical dielectric constant of solvent and ϵ is the static dielectric constant of solvent. The radii of **IV** and *fac*-Ir^{IV}(ppy)₃ are 4.65 Å and 5.2 Å respectively. The ϵ_{op} and ϵ of CH₃CN are 1.807 and 35.688 respectively, and the ϵ_{op} and ϵ of DMA are 2.068 and 37.781 respectively.

B3LYP-D3(BJ)/6-31G(d,p)-SDD(Ir) calculated Cartesian coordinates and energies.

1a

C	0.52314	0.45327	-0.83918
C	-0.64983	0.29946	-0.57363
C	-2.03188	0.11409	-0.26735
C	-2.61609	-1.16323	-0.3522
C	-2.82911	1.20432	0.1272
C	-3.96278	-1.341	-0.0499
H	-2.00255	-2.00461	-0.65594
C	-4.17511	1.01788	0.42739
H	-2.37991	2.18945	0.19326
C	-4.74621	-0.25319	0.34029
H	-4.40265	-2.33112	-0.1188
H	-4.78064	1.86649	0.73039
H	-5.79638	-0.39529	0.57538
C	1.94348	0.63191	-1.1258
H	2.22677	0.02036	-1.99212
H	2.13016	1.6755	-1.41076
C	2.89659	0.29227	0.06409
C	4.34662	0.52651	-0.36124
H	5.03162	0.25675	0.44562
H	4.60655	-0.08578	-1.22903
H	4.50481	1.57909	-0.61613
C	2.52839	1.14957	1.29038
H	2.62083	2.21231	1.04329
H	1.49858	0.96648	1.60899
H	3.19807	0.93516	2.12844
C	2.68265	-1.16756	0.44494
O	3.55653	-2.00601	0.47992
H	1.63328	-1.42252	0.70812

Zero-point correction = 0.232517 (Hartree/Particle)

Thermal correction to Energy = 0.246662

Thermal correction to Enthalpy = 0.247606

Thermal correction to Gibbs Free Energy = 0.188413

Corrected correction to Gibbs Free Energy = 0.192732

wb97xd/def2tzvp-SMD(MeCN): E = -579.009382772 hartree

wb97xd/def2tzvp-SMD(DMA): E = -579.008219 hartree

Ts·

S	-2.16336	-0.00028	-0.24162
O	-2.64889	1.30357	0.2912
O	-2.64804	-1.30433	0.2915
C	-0.36442	0.00027	-0.09311
C	0.31318	-1.21806	-0.07987
C	0.31231	1.21854	-0.07968
C	1.70339	-1.20533	-0.01951
H	-0.24267	-2.14832	-0.09748
C	1.70304	1.20649	-0.01925
H	-0.24383	2.14863	-0.0972
C	2.41755	0.001	0.01277
H	2.24437	-2.14687	0.00423
H	2.24349	2.14824	0.00477
C	3.92162	-0.00043	0.10691
H	4.34968	0.91216	-0.3159
H	4.24441	-0.06058	1.15324
H	4.3536	-0.8576	-0.41681

Zero-point correction = 0.126163 (Hartree/Particle)

Thermal correction to Energy = 0.135662

Thermal correction to Enthalpy = 0.136606

Thermal correction to Gibbs Free Energy = 0.089286

Corrected correction to Gibbs Free Energy = 0.092438

wb97xd/def2tzvp-SMD(MeCN): E = -819.591447268 hartree

wb97xd/def2tzvp-SMD(DMA): E = -819.592291 hartree

3a

C	3.47924	0.22114	0.64653
C	2.36141	1.27377	0.52557
C	1.18759	0.66063	-0.17424
C	1.47545	-0.64091	-0.38323
C	2.86419	-1.05639	0.02332
H	3.42674	-1.40705	-0.84993
H	2.82491	-1.89915	0.71929
C	3.81421	0.03239	2.13406
H	4.63591	-0.68	2.25527
H	4.10703	0.98913	2.57424
H	2.94899	-0.34704	2.6877
C	4.70878	0.72126	-0.12761
H	5.0331	1.68743	0.26799
H	5.53408	0.00835	-0.03601
H	4.48182	0.84633	-1.19124

O	2.41891	2.40816	0.95693
C	-0.02506	1.4243	-0.49808
C	-0.6819	2.15366	0.50323
C	-0.52456	1.44704	-1.80841
C	-1.84652	2.8559	0.20543
H	-0.28244	2.15508	1.51062
C	-1.67642	2.17154	-2.10552
H	-0.01553	0.88185	-2.58082
C	-2.34578	2.86746	-1.09854
H	-2.35976	3.40379	0.98966
H	-2.05508	2.18496	-3.12284
H	-3.24873	3.42442	-1.32957
S	0.34042	-1.90116	-0.9828
O	0.11887	-1.71204	-2.42653
O	0.87159	-3.17211	-0.46342
C	-1.16929	-1.50993	-0.11258
C	-1.19972	-1.6451	1.27528
C	-2.25934	-1.00586	-0.81617
C	-2.33401	-1.23237	1.96613
H	-0.34857	-2.06383	1.80126
C	-3.38755	-0.60244	-0.10951
H	-2.20386	-0.91654	-1.89329
C	-3.43507	-0.69127	1.28721
H	-2.36673	-1.32595	3.04762
H	-4.23623	-0.19326	-0.64907
C	-4.63307	-0.18028	2.04467
H	-4.56381	0.90575	2.18149
H	-5.56298	-0.38094	1.5051
H	-4.70614	-0.63408	3.03631

Zero-point correction = 0.354288 (Hartree/Particle)

Thermal correction to Energy = 0.376845

Thermal correction to Enthalpy = 0.377790

Thermal correction to Gibbs Free Energy = 0.300642

Corrected correction to Gibbs Free Energy = 0.30472

wb97xd/def2tzvp-SMD(MeCN): E = -1398.10068687 hartree

wb97xd/def2tzvp-SMD(DMA): E = 0.304719 hartree

4a

C	3.7112	-0.2834	-0.51696
C	2.61533	-1.29547	-0.16113
C	1.31924	-0.60372	0.16493
C	1.04084	0.65116	-0.20884
C	2.0475	1.40437	-1.06436
H	2.45499	-1.99042	-0.99332

O	2.4076	2.56137	-0.33317
H	3.04694	3.03983	-0.87908
C	-0.18673	1.41429	0.12461
C	-0.44571	1.80233	1.44453
C	-1.08154	1.78509	-0.88812
C	-1.59067	2.53752	1.74592
H	0.2424	1.50712	2.22704
C	-2.23119	2.5078	-0.58179
H	-0.89515	1.47211	-1.91062
C	-2.48728	2.88828	0.73661
H	-1.78355	2.83206	2.77284
H	-2.92853	2.77133	-1.37112
H	-3.38224	3.45478	0.97524
S	0.15655	-1.6448	1.08486
O	0.57914	-3.02833	0.8033
O	0.06312	-1.1702	2.47702
C	-1.42501	-1.38025	0.29296
C	-2.45965	-0.79049	1.01243
C	-1.59039	-1.76185	-1.03737
C	-3.67206	-0.55272	0.37362
H	-2.29513	-0.50516	2.04363
C	-2.8068	-1.50843	-1.66341
H	-0.78012	-2.24664	-1.57112
C	-3.85879	-0.89141	-0.97239
H	-4.48049	-0.07979	0.92318
H	-2.94518	-1.79427	-2.70216
C	-5.15469	-0.56558	-1.66945
H	-5.29824	-1.18179	-2.56077
H	-6.01286	-0.71433	-1.00773
H	-5.16832	0.48419	-1.98746
H	2.9329	-1.91069	0.68575
C	4.84451	-0.9661	-1.27591
H	5.62044	-0.23944	-1.53163
H	5.29295	-1.75377	-0.66368
H	4.46832	-1.41081	-2.20085
C	4.24926	0.42956	0.72934
H	4.779	-0.2889	1.36249
H	4.95046	1.21465	0.43534
H	3.45264	0.88925	1.31436
O	3.15606	0.65547	-1.47532
H	1.55252	1.69518	-2.00404

Zero-point correction = 0.382395 (Hartree/Particle)

Thermal correction to Energy = 0.406044

Thermal correction to Enthalpy = 0.406988

Thermal correction to Gibbs Free Energy = 0.329256
 Corrected correction to Gibbs Free Energy = 0.332569
 wb97xd/def2tzvp-SMD(MeCN): E = -1474.53481164 hartree
 wb97xd/def2tzvp-SMD(DMA): E = 0.332568 hartree

MeCN

C	1.18012	-0.00002	-0.00002
H	1.55824	-0.89049	-0.50947
H	1.55842	0.8864	-0.51636
H	1.55844	0.00393	1.02581
C	-0.27961	0.00008	0.00003
N	-1.43973	-0.00003	-0.00001

Zero-point correction = 0.045445 (Hartree/Particle)
 Thermal correction to Energy = 0.049047
 Thermal correction to Enthalpy = 0.049991
 Thermal correction to Gibbs Free Energy = 0.021427
 Corrected correction to Gibbs Free Energy = 0.027216
 wb97xd/def2tzvp-SMD(MeCN): E = -132.766806873 hartree

DMA

C	-0.72812	-0.29362	-0.00002
O	-1.06685	-1.47282	0.00005
N	0.59504	0.08313	-0.00013
C	-1.77326	0.81401	-0.00001
H	-1.69203	1.45285	0.88512
H	-1.69216	1.45276	-0.88521
H	-2.74937	0.33132	0.00009
C	1.07946	1.44922	0.00005
H	1.69792	1.64088	0.88705
H	1.69871	1.64075	-0.88642
H	0.25733	2.16122	-0.00038
C	1.62198	-0.94533	0.
H	2.25851	-0.85431	0.88922
H	1.13125	-1.91659	-0.00029
H	2.25902	-0.85395	-0.8888

Zero-point correction = 0.130573 (Hartree/Particle)
 Thermal correction to Energy = 0.138301
 Thermal correction to Enthalpy = 0.139245
 Thermal correction to Gibbs Free Energy = 0.098567
 Corrected correction to Gibbs Free Energy = 0.103735
 wb97xd/def2tzvp-SMD(DMA): E = -287.862329634 hartree

fac-Ir^{IV}(ppy)₃

C	2.00721	-1.93945	0.79602
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C	1.74133	-0.28324	2.44885
C	2.76362	-0.81939	3.21835
C	3.42769	-1.9543	2.74969
C	3.04772	-2.51194	1.53479
C	1.5081	-2.42957	-0.49374
C	0.47146	-1.67389	-1.0949
C	-0.02803	-2.06596	-2.33926
C	0.4572	-3.21884	-2.96239
C	1.46615	-3.97409	-2.356
C	1.99038	-3.58427	-1.12528
H	1.18706	0.59524	2.75394
H	3.02776	-0.3537	4.16029
H	4.23261	-2.3993	3.32513
H	3.5538	-3.39049	1.15483
H	-0.80886	-1.48413	-2.81982
H	0.04923	-3.53089	-3.91912
H	1.84475	-4.86601	-2.84401
H	2.76918	-4.18538	-0.66682
C	0.81727	2.77126	0.54061
C	0.86307	4.04566	1.13062
C	-0.05253	4.39118	2.11806
C	-1.02302	3.46881	2.51755
C	-1.0776	2.19922	1.93429
C	-0.15121	1.83381	0.94811
C	1.73494	2.34058	-0.51684
C	2.77764	3.12101	-1.03487
C	3.57976	2.62176	-2.0516
C	3.32982	1.34038	-2.54547
C	2.2884	0.61056	-1.99019
H	1.60668	4.77267	0.82059
H	-0.01486	5.37614	2.57122
H	-1.74382	3.73688	3.28474
H	-1.83864	1.49705	2.25714
H	2.95479	4.11258	-0.63815
H	4.38795	3.22302	-2.45516
H	3.92558	0.91003	-3.34182
H	2.05528	-0.38691	-2.33869
C	-2.92053	0.08422	-0.8057
C	-1.54251	1.34836	-2.23265
C	-2.62376	1.7322	-3.01334
C	-3.89466	1.26775	-2.66968
C	-4.04088	0.44234	-1.56045
C	-2.91371	-0.76367	0.38696
C	-1.63002	-0.97861	0.97823

C	-1.55359	-1.78976	2.12793
C	-2.70051	-2.35546	2.67767
C	-3.95132	-2.12965	2.08881
C	-4.05803	-1.33648	0.94502
H	-0.53278	1.67687	-2.44243
H	-2.4676	2.38211	-3.86601
H	-4.76164	1.54874	-3.25802
H	-5.01906	0.07518	-1.27554
H	-0.59083	-1.9757	2.5911
H	-2.6277	-2.97668	3.56493
H	-4.8424	-2.57317	2.5204
H	-5.03513	-1.17404	0.50154
N	1.50855	1.08836	-1.00319
N	1.37319	-0.82791	1.27442
N	-1.68667	0.54234	-1.16697
Ir	-0.13423	-0.06614	0.05889

Zero-point correction = 0.482659 (Hartree/Particle)

Thermal correction to Energy = 0.511561

Thermal correction to Enthalpy = 0.512505

Thermal correction to Gibbs Free Energy = 0.421798

Corrected correction to Gibbs Free Energy = 0.425634

wb97xd/def2tzvp-SMD(MeCN): E = -1540.62049560 hartree

wb97xd/def2tzvp-SMD(DMA): E = -1540.61593 hartree

fac-Ir^{III}(ppy)₃

C	-2.06594	1.94449	0.74538
C	-1.94634	0.16697	2.28472
C	-2.98038	0.68698	3.04811
C	-3.57747	1.88075	2.63608
C	-3.11747	2.5045	1.48563
C	-1.48505	2.51559	-0.47066
C	-0.39492	1.78948	-1.02153
C	0.19092	2.31319	-2.18538
C	-0.27678	3.48688	-2.7783
C	-1.35693	4.18201	-2.22013
C	-1.95972	3.69708	-1.06519
H	-1.43662	-0.75044	2.54977
H	-3.30296	0.16572	3.94196
H	-4.38915	2.31966	3.20803
H	-3.56226	3.43428	1.15301
H	1.03548	1.79501	-2.63496
H	0.20008	3.86867	-3.67818
H	-1.72052	5.09459	-2.68264
H	-2.79649	4.24192	-0.63595

C	-0.65693	-2.83184	0.51697
C	-0.66168	-4.11916	1.08412
C	0.18724	-4.41862	2.14261
C	1.04659	-3.42971	2.6359
C	1.05178	-2.15362	2.07127
C	0.20625	-1.80938	1.00196
C	-1.54157	-2.46726	-0.59759
C	-2.48695	-3.31948	-1.1922
C	-3.27377	-2.86684	-2.24186
C	-3.1185	-1.55564	-2.69894
C	-2.17256	-0.75337	-2.07584
H	-1.3225	-4.8938	0.70448
H	0.18321	-5.41265	2.57976
H	1.71447	-3.66058	3.46271
H	1.72815	-1.40094	2.46822
H	-2.60146	-4.33189	-0.82521
H	-4.00376	-3.52791	-2.6992
H	-3.71406	-1.1606	-3.51403
H	-2.00014	0.27424	-2.37641
C	2.88919	0.00957	-0.71114
C	1.61661	-1.22006	-2.26246
C	2.73658	-1.53353	-3.01491
C	3.98052	-1.05463	-2.59104
C	4.05095	-0.28565	-1.43975
C	2.81524	0.80526	0.50552
C	1.50499	0.96599	1.03807
C	1.38154	1.72819	2.21319
C	2.49513	2.29295	2.83089
C	3.77855	2.11982	2.29405
C	3.93536	1.37733	1.13156
H	0.62723	-1.56321	-2.53628
H	2.63303	-2.13995	-3.90726
H	4.8806	-1.28105	-3.15383
H	5.0033	0.09634	-1.09251
H	0.39963	1.88133	2.65089
H	2.36815	2.87669	3.73948
H	4.64188	2.56257	2.78093
H	4.92976	1.24296	0.71434
N	-1.40555	-1.19203	-1.06335
N	-1.49895	0.77088	1.16687
N	1.68197	-0.47009	-1.14611
Ir	0.05579	0.034	0.00632

Zero-point correction = 0.481255 (Hartree/Particle)

Thermal correction to Energy = 0.509990

Thermal correction to Enthalpy = 0.510934
 Thermal correction to Gibbs Free Energy = 0.421263
 Corrected correction to Gibbs Free Energy = 0.42519
 wb97xd/def2tzvp-SMD(MeCN): E = -1540.79632964 hartree
 wb97xd/def2tzvp-SMD(DMA): E = -1540.791721 hartree

H₂O

O	0.	0.	0.11919
H	0.	0.75927	-0.47675
H	0.	-0.75927	-0.47675

Zero-point correction = 0.021370 (Hartree/Particle)
 Thermal correction to Energy = 0.024205
 Thermal correction to Enthalpy = 0.025149
 Thermal correction to Gibbs Free Energy = 0.003713
 Corrected correction to Gibbs Free Energy = 0.006732
 wb97xd/def2tzvp-SMD(MeCN): E = -76.4459585894 hartree
 wb97xd/def2tzvp-SMD(DMA): E = -76.445828 hartree

I

C	-1.37577	-0.15366	-0.75239
C	-0.55781	0.85215	-0.6795
C	0.64765	1.53562	-0.58519
C	1.34011	1.96007	-1.75467
C	1.22064	1.82288	0.68582
C	2.56001	2.60684	-1.64688
H	0.90505	1.74916	-2.72526
C	2.44189	2.47068	0.77053
H	0.70035	1.50081	1.58014
C	3.12191	2.86352	-0.38918
H	3.08422	2.914	-2.54647
H	2.87397	2.67142	1.74609
H	4.07778	3.37154	-0.31392
C	-2.88986	-0.16187	-0.77963
H	-3.23291	0.44081	-1.6265
H	-3.23311	-1.18589	-0.95129
C	-3.57785	0.34109	0.52559
C	-5.08607	0.10552	0.40429
H	-5.60929	0.50953	1.27409
H	-5.49242	0.60135	-0.4813
H	-5.29728	-0.96557	0.33446
C	-3.00252	-0.38236	1.75821
H	-3.06587	-1.46458	1.62393
H	-1.9482	-0.13184	1.91149
H	-3.55498	-0.10021	2.65944

C	-3.29397	1.8291	0.68561
O	-4.136	2.70005	0.69175
H	-2.21742	2.08263	0.80892
S	-0.64276	-1.8583	-0.84944
O	-1.44558	-2.72004	0.0401
O	-0.47453	-2.21157	-2.26951
C	0.97263	-1.63787	-0.12257
C	2.05172	-1.32676	-0.94764
C	1.10309	-1.67235	1.26408
C	3.27533	-1.01671	-0.36508
H	1.91832	-1.31719	-2.02296
C	2.33704	-1.3624	1.82961
H	0.25051	-1.9385	1.87885
C	3.43112	-1.01171	1.02752
H	4.1178	-0.75446	-0.99791
H	2.45217	-1.38332	2.9094
C	4.74051	-0.59394	1.64347
H	4.8114	-0.902	2.68953
H	5.59164	-1.01708	1.10194
H	4.84246	0.49749	1.60768

Zero-point correction = 0.361445 (Hartree/Particle)

Thermal correction to Energy = 0.385608

Thermal correction to Enthalpy = 0.386553

Thermal correction to Gibbs Free Energy = 0.304555

Corrected correction to Gibbs Free Energy = 0.30876

wb97xd/def2tzvp-SMD(MeCN): E = -1398.61938419 hartree

wb97xd/def2tzvp-SMD(DMA): E = -1398.6193 hartree

II

C	-3.5448	0.38404	-0.49867
C	-2.34076	1.33549	-0.76339
C	-1.17713	0.68842	0.04152
C	-1.49091	-0.60576	0.22863
C	-2.8597	-0.99118	-0.26492
H	-3.39956	-1.61123	0.45746
H	-2.77739	-1.57919	-1.18518
C	-4.51491	0.3597	-1.68014
H	-5.30283	-0.38215	-1.51485
H	-4.99687	1.33436	-1.81298
H	-3.98886	0.10969	-2.60459
C	-4.25359	0.83639	0.78464
H	-4.65817	1.84788	0.6717
H	-5.08657	0.16665	1.01965
H	-3.57055	0.8367	1.64022

O	-1.8213	1.28005	-2.02933
C	0.03094	1.4374	0.40859
C	0.79089	2.10009	-0.56706
C	0.42941	1.49665	1.75332
C	1.95	2.78004	-0.20397
H	0.46615	2.05974	-1.60041
C	1.58132	2.19364	2.11049
H	-0.15335	0.97497	2.50379
C	2.34808	2.82926	1.13381
H	2.54207	3.27686	-0.96647
H	1.88275	2.23289	3.15263
H	3.24936	3.36623	1.41339
S	-0.40788	-1.8596	0.91672
O	-0.2669	-1.65385	2.36892
O	-0.92024	-3.13398	0.38717
C	1.15792	-1.49287	0.1369
C	1.26227	-1.60285	-1.24942
C	2.21862	-1.02993	0.90973
C	2.44457	-1.21051	-1.86749
H	0.4283	-1.97855	-1.83209
C	3.39608	-0.64695	0.2752
H	2.10245	-0.95462	1.98339
C	3.5204	-0.71409	-1.11782
H	2.53373	-1.28233	-2.94742
H	4.22378	-0.27055	0.86879
C	4.77189	-0.22267	-1.79802
H	4.7298	0.8646	-1.93697
H	5.6631	-0.43991	-1.20246
H	4.89857	-0.67619	-2.78443
H	-2.51566	2.37411	-0.43635

Zero-point correction = 0.364139 (Hartree/Particle)

Thermal correction to Energy = 0.386835

Thermal correction to Enthalpy = 0.387779

Thermal correction to Gibbs Free Energy = 0.311006

Corrected correction to Gibbs Free Energy = 0.314384

wb97xd/def2tzvp-SMD(MeCN): E = -1398.62508370 hartree

wb97xd/def2tzvp-SMD(DMA): E = -1398.625062 hartree

III

C	3.35355	0.17816	0.74289
C	2.26828	1.19294	0.47244
C	1.19666	0.67923	-0.23839
C	1.48466	-0.6637	-0.55842
C	2.87089	-1.04479	-0.10648

H	3.53241	-1.20367	-0.96809
H	2.87132	-1.97894	0.46183
C	3.36149	-0.16657	2.24686
H	4.12419	-0.92244	2.45895
H	3.57689	0.72197	2.84732
H	2.38918	-0.56324	2.55567
C	4.73444	0.68776	0.3051
H	5.01572	1.58134	0.8693
H	5.49398	-0.08142	0.47692
H	4.73811	0.94052	-0.75937
O	2.40643	2.44543	0.95204
C	-0.02911	1.4457	-0.54318
C	-0.74761	2.05468	0.498
C	-0.49321	1.57565	-1.8607
C	-1.91286	2.77173	0.22849
H	-0.41751	1.91663	1.52357
C	-1.65514	2.29564	-2.12533
H	0.04473	1.08139	-2.6612
C	-2.36794	2.89439	-1.08401
H	-2.46929	3.22331	1.04408
H	-2.00946	2.38484	-3.14759
H	-3.27655	3.44971	-1.29523
S	0.33706	-1.84603	-1.16086
O	-0.01958	-1.55527	-2.56402
O	0.87812	-3.16824	-0.79523
C	-1.1212	-1.51672	-0.16881
C	-1.06366	-1.72012	1.20964
C	-2.2566	-0.98039	-0.76977
C	-2.15269	-1.3531	1.99394
H	-0.17708	-2.15739	1.65669
C	-3.33899	-0.62089	0.02775
H	-2.26789	-0.83287	-1.84222
C	-3.29851	-0.78644	1.41757
H	-2.11564	-1.50505	3.06898
H	-4.2226	-0.19001	-0.434
C	-4.45117	-0.3322	2.27625
H	-4.39303	0.74725	2.46308
H	-5.41193	-0.5249	1.79009
H	-4.452	-0.83468	3.24706
H	1.62604	2.96298	0.69266

Zero-point correction = 0.364955 (Hartree/Particle)

Thermal correction to Energy = 0.387947

Thermal correction to Enthalpy = 0.388891

Thermal correction to Gibbs Free Energy = 0.310722

Corrected correction to Gibbs Free Energy = 0.314569
 wb97xd/def2tzvp-SMD(MeCN): E = -1398.67522002 hartree
 wb97xd/def2tzvp-SMD(DMA): E = -1398.67426 hartree

IV

C	1.53239	-0.18171	-0.56421
C	0.99026	1.05948	-0.71723
C	-0.19603	1.5649	0.02689
C	-0.14674	1.76071	1.41374
C	-1.35978	1.92264	-0.66998
C	-1.24943	2.27908	2.0904
H	0.74764	1.48158	1.95721
C	-2.46354	2.43134	0.00918
H	-1.40881	1.76276	-1.7426
C	-2.41069	2.61139	1.39238
H	-1.20001	2.4219	3.16542
H	-3.36497	2.68463	-0.54025
H	-3.26993	3.01052	1.92257
C	2.8654	-0.65341	-1.09424
H	2.81978	-1.71921	-1.32096
H	3.11359	-0.07677	-1.98521
C	3.83267	-0.37205	0.02444
C	4.14315	-1.41429	1.04677
H	3.55054	-1.26637	1.96259
H	3.91846	-2.42014	0.68557
H	5.19885	-1.36145	1.34143
C	4.26074	1.03886	0.2486
H	5.1127	1.09323	0.93231
H	4.51558	1.53523	-0.69413
H	3.45056	1.64024	0.69524
C	1.53264	2.04895	-1.69047
O	2.5219	1.94194	-2.39749
H	0.92105	2.97383	-1.73075
S	0.73484	-1.43853	0.50122
O	1.23339	-2.73979	0.01856
O	0.89912	-1.0786	1.92336
C	-1.00121	-1.3372	0.08861
C	-1.91978	-1.01239	1.0817
C	-1.40436	-1.59556	-1.2206
C	-3.26573	-0.91529	0.74472
H	-1.57012	-0.81541	2.08706
C	-2.75316	-1.4828	-1.54176
H	-0.67502	-1.87381	-1.97355
C	-3.69985	-1.13179	-0.56907

H	-3.98889	-0.64969	1.51003
H	-3.07886	-1.67204	-2.56045
C	-5.15168	-0.95692	-0.93348
H	-5.40758	-1.50864	-1.8417
H	-5.80949	-1.29671	-0.1285
H	-5.3794	0.10072	-1.11467

Zero-point correction = 0.361194 (Hartree/Particle)

Thermal correction to Energy = 0.385322

Thermal correction to Enthalpy = 0.386266

Thermal correction to Gibbs Free Energy = 0.306094

Corrected correction to Gibbs Free Energy = 0.309075

wb97xd/def2tzvp-SMD(MeCN): E = -1398.61710883 hartree

wb97xd/def2tzvp-SMD(DMA): E = -1398.616492 hartree

V

C	1.52802	0.08694	0.66437
C	1.04175	1.14621	-0.10955
C	-0.33689	1.69711	-0.03578
C	-0.84577	2.20281	1.16846
C	-1.13834	1.73532	-1.18456
C	-2.1359	2.72631	1.21977
H	-0.23538	2.15936	2.06247
C	-2.43057	2.25304	-1.12938
H	-0.75249	1.32507	-2.11231
C	-2.93266	2.74989	0.07394
H	-2.52019	3.114	2.15823
H	-3.04668	2.26295	-2.02341
H	-3.93996	3.15271	0.11892
C	2.99284	-0.23058	0.59814
H	3.54872	0.43299	1.27522
H	3.17552	-1.25672	0.92299
C	3.52403	-0.0377	-0.82963
C	5.04562	-0.04657	-0.86272
H	5.40576	0.15305	-1.87536
H	5.44876	0.71769	-0.19337
H	5.42086	-1.02318	-0.54481
C	2.92956	-1.05463	-1.80408
H	3.20259	-2.0689	-1.49924
H	1.83997	-0.98407	-1.82358
H	3.30884	-0.87606	-2.81341
C	1.91163	1.73324	-1.02481
O	3.14955	1.30004	-1.30707
H	1.64553	2.62746	-1.57675
S	0.50844	-0.98354	1.65404

O	1.25556	-2.25242	1.76668
O	0.05989	-0.29151	2.87758
C	-0.93432	-1.27838	0.63525
C	-2.17209	-0.78671	1.03906
C	-0.7876	-1.96611	-0.56868
C	-3.27126	-0.95823	0.20397
H	-2.25187	-0.2593	1.98077
C	-1.89543	-2.12298	-1.39593
H	0.17769	-2.37384	-0.84737
C	-3.14757	-1.61044	-1.02919
H	-4.23692	-0.56372	0.50594
H	-1.79027	-2.65186	-2.33892
C	-4.33242	-1.72943	-1.95314
H	-4.19351	-2.52974	-2.6846
H	-5.25364	-1.92874	-1.39789
H	-4.4843	-0.79593	-2.50879

Zero-point correction = 0.365389 (Hartree/Particle)

Thermal correction to Energy = 0.387727

Thermal correction to Enthalpy = 0.388672

Thermal correction to Gibbs Free Energy = 0.313064

Corrected correction to Gibbs Free Energy = 0.316373

wb97xd/def2tzvp-SMD(MeCN): E = -1398.66550387 hartree

wb97xd/def2tzvp-SMD(DMA): E = -1398.664851 hartree

VI

C	-1.50935	-0.08523	-0.55259
C	-1.06043	1.06826	0.02993
C	0.29679	1.65998	-0.07408
C	0.77863	2.09725	-1.31531
C	1.07346	1.82617	1.07999
C	2.03784	2.6892	-1.39634
H	0.17773	1.96142	-2.20707
C	2.33756	2.40251	0.98823
H	0.70457	1.47363	2.03872
C	2.81818	2.83742	-0.24933
H	2.40826	3.03179	-2.35659
H	2.94461	2.51614	1.87993
H	3.79906	3.29614	-0.31729
C	-2.95953	-0.45312	-0.51317
H	-3.44539	0.00704	-1.38587
H	-3.06787	-1.53412	-0.63451
C	-3.63609	-0.02194	0.78258
C	-5.1445	0.06403	0.65554
H	-5.59034	0.42634	1.58402

H	-5.43489	0.72633	-0.16296
H	-5.53909	-0.93443	0.44945
C	-3.18019	-0.81647	1.99796
H	-3.52734	-1.84765	1.89084
H	-2.09125	-0.83277	2.09152
H	-3.61156	-0.40174	2.91106
C	-2.03635	1.81707	0.75849
O	-3.20526	1.42131	1.07871
H	-1.80365	2.82594	1.10082
S	-0.44072	-1.24588	-1.48979
O	-1.16926	-2.51636	-1.38317
O	-0.17728	-0.60486	-2.78196
C	1.0344	-1.33563	-0.52117
C	2.21726	-0.78515	-1.01541
C	0.97023	-1.93582	0.74075
C	3.35052	-0.81975	-0.21322
H	2.23455	-0.33582	-1.9998
C	2.11283	-1.94618	1.53084
H	0.05129	-2.39828	1.08483
C	3.31602	-1.3874	1.07
H	4.27735	-0.39428	-0.58409
H	2.08014	-2.4058	2.51361
C	4.55647	-1.42663	1.92025
H	4.31433	-1.49585	2.98329
H	5.16612	-2.30106	1.66409
H	5.17709	-0.54107	1.76035

Zero-point correction = 0.366368 (Hartree/Particle)

Thermal correction to Energy = 0.388874

Thermal correction to Enthalpy = 0.389819

Thermal correction to Gibbs Free Energy = 0.313822

Corrected correction to Gibbs Free Energy = 0.317446

wb97xd/def2tzvp-SMD(MeCN): E = -1398.49537737 hartree

wb97xd/def2tzvp-SMD(DMA): E = -1398.494741 hartree

VII

C	1.50816	-0.11058	-0.39852
C	1.01287	1.13722	-0.5527
C	-0.2489	1.62714	0.05344
C	-0.33867	1.81955	1.43962
C	-1.32891	1.9778	-0.77159
C	-1.5046	2.34457	1.99234
H	0.49561	1.55009	2.0757
C	-2.49902	2.47804	-0.20918
H	-1.26648	1.82002	-1.84384

C	-2.58614	2.66721	1.17223
H	-1.56756	2.49885	3.06429
H	-3.33985	2.72636	-0.84795
H	-3.49474	3.07056	1.60689
C	2.80693	-0.62745	-1.01319
H	2.65784	-1.70271	-1.19452
H	3.02846	-0.09394	-1.93536
C	3.92365	-0.4901	-0.03983
C	3.90334	-1.24324	1.20972
H	3.11517	-0.80902	1.85776
H	3.52435	-2.26077	1.04647
H	4.8528	-1.22224	1.74228
C	5.02554	0.40686	-0.36435
H	5.78308	0.49453	0.41187
H	5.47928	0.04917	-1.30556
H	4.59869	1.37721	-0.66411
C	1.69463	2.15865	-1.41989
O	2.87426	2.15566	-1.71767
H	1.02141	2.96468	-1.76392
S	0.64555	-1.41023	0.57508
O	1.24219	-2.66656	0.07459
O	0.80403	-1.04802	1.99658
C	-1.05676	-1.33872	0.10323
C	-2.00908	-0.97159	1.05265
C	-1.40584	-1.65882	-1.21077
C	-3.34063	-0.90238	0.661
H	-1.70401	-0.73874	2.06454
C	-2.74222	-1.57139	-1.58112
H	-0.65317	-1.97927	-1.92281
C	-3.72635	-1.18542	-0.65725
H	-4.09368	-0.61892	1.38925
H	-3.03137	-1.81677	-2.59805
C	-5.16634	-1.0569	-1.07564
H	-5.38241	-1.65546	-1.96331
H	-5.8426	-1.36826	-0.27545
H	-5.4034	-0.01316	-1.31463

Zero-point correction = 0.361132 (Hartree/Particle)

Thermal correction to Energy = 0.384143

Thermal correction to Enthalpy = 0.385087

Thermal correction to Gibbs Free Energy = 0.308070

Corrected correction to Gibbs Free Energy = 0.312234

wb97xd/def2tzvp-SMD(CH₃CN): E = -1398.45386427 hartree

wb97xd/def2tzvp-SMD(DMAc): E = -1398.45302536 hartree

TS1

C	1.47012	0.22511	0.86901
C	0.50628	1.01073	0.80079
C	-0.76077	1.61545	0.70578
C	-1.50348	1.928	1.86815
C	-1.32292	1.88926	-0.56231
C	-2.77487	2.47412	1.75662
H	-1.07181	1.71712	2.84027
C	-2.59287	2.44054	-0.65801
H	-0.75828	1.6412	-1.45339
C	-3.32595	2.73085	0.49685
H	-3.34229	2.70134	2.65356
H	-3.01797	2.64171	-1.63629
H	-4.31977	3.15957	0.41615
C	2.93566	0.00507	0.83654
H	3.39734	0.5733	1.65252
H	3.15791	-1.05158	1.01342
C	3.60718	0.3933	-0.51771
C	5.08945	0.01727	-0.45684
H	5.60154	0.33502	-1.36769
H	5.58673	0.50617	0.38544
H	5.20161	-1.06559	-0.34977
C	2.90205	-0.32325	-1.68664
H	2.8864	-1.40143	-1.508
H	1.865	0.01054	-1.79031
H	3.4234	-0.12354	-2.62733
C	3.45029	1.8928	-0.73358
O	4.36633	2.66732	-0.9029
H	2.39673	2.24911	-0.74008
S	0.59648	-1.94053	0.97397
O	1.48414	-2.79449	0.13703
O	0.2598	-2.33445	2.3652
C	-0.94483	-1.70048	0.08925
C	-2.09051	-1.37185	0.81282
C	-0.93532	-1.68615	-1.30325
C	-3.24698	-1.03014	0.12154
H	-2.06244	-1.38368	1.8959
C	-2.10411	-1.34051	-1.97841
H	-0.0309	-1.94989	-1.83964
C	-3.26832	-0.99706	-1.27947
H	-4.1417	-0.76343	0.67614
H	-2.11206	-1.33217	-3.06458
C	-4.51564	-0.56858	-2.00767
H	-4.42045	-0.70876	-3.08711

H	-5.39003	-1.13209	-1.66674
H	-4.7216	0.49185	-1.82133

Zero-point correction = 0.359765 (Hartree/Particle)
Thermal correction to Energy = 0.384095
Thermal correction to Enthalpy = 0.385040
Thermal correction to Gibbs Free Energy = 0.302772
Corrected correction to Gibbs Free Energy = 0.306676
wb97xd/def2tzvp-SMD(MeCN): E = -1398.59935915 hartree
wb97xd/def2tzvp-SMD(DMA): E = -1398.599313 hartree

TS2

C	-1.48026	-0.65095	-0.07131
C	-1.0145	0.57256	0.04503
C	0.14134	1.40579	0.13381
C	0.44609	2.2965	-0.91781
C	0.96677	1.37583	1.27588
C	1.58174	3.09235	-0.84455
H	-0.22953	2.35179	-1.76349
C	2.10426	2.17193	1.33319
H	0.72051	0.70343	2.08923
C	2.41861	3.02754	0.27434
H	1.81573	3.77058	-1.65901
H	2.74868	2.12473	2.20522
H	3.30459	3.65277	0.32685
C	-2.9703	-0.87132	-0.16803
H	-3.22263	-1.05839	-1.21723
H	-3.27992	-1.74917	0.40757
C	-3.64195	0.41835	0.35384
C	-5.04503	0.57946	-0.24697
H	-5.54876	1.46194	0.16064
H	-4.97981	0.69299	-1.33154
H	-5.66182	-0.29572	-0.01779
C	-3.70028	0.40398	1.88648
H	-4.35975	-0.39449	2.23901
H	-2.71026	0.24175	2.32314
H	-4.08873	1.35339	2.27008
C	-2.75038	1.59767	-0.11422
O	-2.70826	1.94542	-1.32095
H	-2.50777	2.34563	0.66912
S	-0.48622	-2.15443	-0.24975
O	-0.74064	-2.98396	0.94037
O	-0.77835	-2.67208	-1.59664
C	1.20769	-1.60521	-0.19682
C	1.7426	-0.93761	-1.29908

C	1.94949	-1.80507	0.9638
C	3.03064	-0.42611	-1.21168
H	1.14946	-0.81311	-2.19786
C	3.24617	-1.29989	1.02645
H	1.50618	-2.34256	1.7942
C	3.79396	-0.58581	-0.04556
H	3.44925	0.11676	-2.05365
H	3.83565	-1.44707	1.92666
C	5.15997	0.03972	0.05628
H	5.73215	-0.37384	0.89033
H	5.73706	-0.10462	-0.86191
H	5.0674	1.12086	0.21575

Zero-point correction = 0.361582 (Hartree/Particle)

Thermal correction to Energy = 0.384397

Thermal correction to Enthalpy = 0.385342

Thermal correction to Gibbs Free Energy = 0.308156

Corrected correction to Gibbs Free Energy = 0.311504

wb97xd/def2tzvp-SMD(MeCN): E = -1398.60720375 hartree

wb97xd/def2tzvp-SMD(DMA): E = -1398.607183 hartree

TS3-NCMe

C	2.75515	-1.5443	0.94207
C	2.27396	-0.06913	0.83041
C	1.0045	-0.09147	0.00431
C	0.86273	-1.32278	-0.52973
C	2.01688	-2.24883	-0.22681
H	2.66284	-2.33748	-1.11035
H	1.67422	-3.25693	0.0195
C	2.23846	-2.07794	2.29059
H	2.54568	-3.1184	2.43749
H	2.63387	-1.47014	3.10837
H	1.14471	-2.03377	2.33215
C	4.27783	-1.65622	0.86981
H	4.73221	-1.03652	1.64881
H	4.60507	-2.69064	1.01741
H	4.65674	-1.31483	-0.09896
O	2.51708	0.81197	1.71053
C	0.17219	1.1087	-0.13768
C	-0.25963	1.79448	1.00818
C	-0.14633	1.6186	-1.40616
C	-1.03234	2.94667	0.88508
H	0.01686	1.41453	1.98396
C	-0.89939	2.78569	-1.5235
H	0.18581	1.08446	-2.2888

C	-1.35127	3.44755	-0.37937
H	-1.38028	3.45973	1.77643
H	-1.14367	3.17073	-2.50889
H	-1.94785	4.35013	-0.47248
S	-0.55355	-1.91177	-1.44108
O	-0.59653	-1.28513	-2.77627
O	-0.5364	-3.37867	-1.30778
C	-1.92122	-1.2656	-0.48217
C	-2.10974	-1.72924	0.82003
C	-2.72312	-0.26096	-1.01398
C	-3.10269	-1.15237	1.60385
H	-1.48178	-2.52264	1.21085
C	-3.71493	0.30445	-0.2167
H	-2.54704	0.0796	-2.02631
C	-3.91372	-0.12412	1.10078
H	-3.25041	-1.49875	2.62275
H	-4.33256	1.10213	-0.61875
C	-4.99346	0.48958	1.95506
H	-5.18599	1.527	1.66809
H	-5.93641	-0.06025	1.8489
H	-4.72314	0.4712	3.01453
H	3.02248	0.49468	-0.29315
C	3.10725	2.53329	-0.68213
N	3.45477	1.46565	-1.02934
C	2.54123	3.72832	-0.08497
H	1.59345	3.9577	-0.58066
H	2.33984	3.50559	0.96818
H	3.22149	4.57988	-0.17017

Zero-point correction = 0.404631 (Hartree/Particle)

Thermal correction to Energy = 0.432070

Thermal correction to Enthalpy = 0.433014

Thermal correction to Gibbs Free Energy = 0.344586

Corrected correction to Gibbs Free Energy = 0.348444

wb97xd/def2tzvp-SMD(MeCN): E = -1531.37431851 hartree

TS3-2H₂O

C	2.91401	-1.18324	0.96062
C	2.33769	0.237	0.72178
C	1.03657	0.04805	-0.00036
C	0.96721	-1.22798	-0.45155
C	2.19882	-2.03755	-0.12224
H	2.82657	-2.14701	-1.01749
H	1.94801	-3.04734	0.21273
C	2.46791	-1.6303	2.36424

H	2.85042	-2.63057	2.59233
H	2.83856	-0.92781	3.11479
H	1.37495	-1.65693	2.43316
C	4.43868	-1.207	0.85109
H	4.87273	-0.50289	1.56715
H	4.83598	-2.20487	1.06411
H	4.76979	-0.9154	-0.15125
O	2.5623	1.20257	1.56335
C	0.10556	1.16864	-0.20136
C	-0.37387	1.87806	0.91046
C	-0.24501	1.59499	-1.49158
C	-1.21027	2.97851	0.7324
H	-0.07853	1.56173	1.90382
C	-1.06407	2.7096	-1.66558
H	0.09459	1.02307	-2.34897
C	-1.5511	3.4017	-0.55522
H	-1.58844	3.51314	1.59811
H	-1.32969	3.03149	-2.66775
H	-2.19323	4.26633	-0.69117
S	-0.39625	-1.95266	-1.32921
O	-0.47308	-1.38578	-2.69202
O	-0.28006	-3.40838	-1.13907
C	-1.81323	-1.35997	-0.40814
C	-1.96885	-1.7601	0.91964
C	-2.69179	-0.4567	-0.99705
C	-3.00892	-1.22191	1.66849
H	-1.27906	-2.47409	1.35669
C	-3.73041	0.07131	-0.23378
H	-2.53974	-0.16266	-2.02782
C	-3.89997	-0.29505	1.10614
H	-3.13228	-1.51929	2.70596
H	-4.4105	0.7897	-0.68187
C	-5.03058	0.27393	1.92473
H	-4.73771	0.4092	2.96987
H	-5.35949	1.24006	1.53286
H	-5.89743	-0.39769	1.91407
H	2.94823	0.78065	-0.45202
O	2.43952	3.39486	0.1483
H	2.42098	2.69812	0.87439
H	1.50604	3.59343	-0.01296
O	3.32549	1.58845	-1.34824
H	2.74259	1.43817	-2.10854
H	2.99312	2.45824	-0.86781

Zero-point correction = 0.409598 (Hartree/Particle)

Thermal correction to Energy = 0.436452
 Thermal correction to Enthalpy = 0.437396
 Thermal correction to Gibbs Free Energy = 0.350736
 Corrected correction to Gibbs Free Energy = 0.354796
 wb97xd/def2tzvp-SMD(MeCN): E = -1551.52819149 hartree
 wb97xd/def2tzvp-SMD(DMA): E = -1551.527652 hartree

TS3-DMA

C	1.98262	2.61737	-0.86219
C	1.79666	1.15146	-1.35027
C	0.62394	0.59831	-0.58573
C	0.3795	1.42091	0.47283
C	1.34217	2.58772	0.54649
H	2.10411	2.39057	1.31355
H	0.84074	3.51859	0.82283
C	1.17203	3.52365	-1.80511
H	1.26748	4.57582	-1.51533
H	1.5292	3.40464	-2.83164
H	0.10977	3.25744	-1.78219
C	3.45299	3.03426	-0.86145
H	3.87413	2.8917	-1.86123
H	3.56829	4.08731	-0.58311
H	4.03685	2.43035	-0.15938
O	2.15346	0.7725	-2.52835
C	0.0118	-0.68516	-0.96122
C	-0.16399	-0.9825	-2.32458
C	-0.33733	-1.65816	-0.00807
C	-0.68981	-2.21065	-2.71818
H	0.1452	-0.25153	-3.05989
C	-0.8575	-2.88713	-0.40849
H	-0.19998	-1.44629	1.04486
C	-1.03559	-3.16932	-1.76402
H	-0.82416	-2.42263	-3.77458
H	-1.13481	-3.62237	0.34187
H	-1.4426	-4.12726	-2.07401
S	-0.78945	1.22	1.77944
O	-0.39049	0.09532	2.66786
O	-0.98643	2.55011	2.38214
C	-2.30106	0.72118	0.95631
C	-2.76805	1.46294	-0.12869
C	-2.99985	-0.38713	1.42326
C	-3.93895	1.06695	-0.76428
H	-2.21337	2.32734	-0.47698
C	-4.17688	-0.76567	0.78155

H	-2.6098	-0.94412	2.26698
C	-4.65713	-0.05479	-0.32391
H	-4.303	1.63329	-1.61673
H	-4.7257	-1.63264	1.13809
C	-5.9025	-0.49807	-1.04839
H	-5.64631	-1.07963	-1.94219
H	-6.53128	-1.12841	-0.41421
H	-6.49838	0.35796	-1.37839
H	2.71232	0.432	-0.51974
C	3.02675	-1.47427	0.22138
O	3.30389	-0.23075	0.31468
N	2.79701	-2.15241	1.34588
C	2.98018	-2.13963	-1.12725
H	3.89711	-2.71988	-1.28323
H	2.12021	-2.803	-1.22605
H	2.91474	-1.36392	-1.89274
C	2.42943	-3.56407	1.35773
H	2.85402	-4.0333	2.24736
H	1.34055	-3.67958	1.3751
H	2.82244	-4.0724	0.47949
C	2.69455	-1.41363	2.61416
H	1.71247	-0.93657	2.70407
H	2.84003	-2.11663	3.43499
H	3.46447	-0.64481	2.64827

Zero-point correction = 0.491869 (Hartree/Particle)

Thermal correction to Energy = 0.523220

Thermal correction to Enthalpy = 0.524164

Thermal correction to Gibbs Free Energy = 0.427275

Corrected correction to Gibbs Free Energy = 0.431197

wb97xd/def2tzvp-SMD(DMA): E = -1686.49295155 hartree

TS4

C	3.69685	0.20338	0.46306
C	2.19469	1.48562	0.81857
C	1.17507	0.72632	-0.0267
C	1.49059	-0.55745	-0.24569
C	2.83541	-1.03031	0.24665
H	3.30569	-1.70298	-0.48187
H	2.71826	-1.60634	1.17028
C	4.57163	0.21405	1.68543
H	5.37486	-0.52613	1.56175
H	5.03892	1.19109	1.83453
H	4.00127	-0.03841	2.58069
C	4.32317	0.75438	-0.79528

H	4.77007	1.73811	-0.62887
H	5.12593	0.07749	-1.12037
H	3.59977	0.82412	-1.61174
O	2.0293	1.49857	2.07347
C	-0.05481	1.44155	-0.41618
C	-0.83552	2.06403	0.5699
C	-0.44484	1.52505	-1.76058
C	-2.01	2.72247	0.21768
H	-0.52072	2.00422	1.60618
C	-1.61007	2.2055	-2.10841
H	0.15347	1.03356	-2.5188
C	-2.39905	2.79706	-1.1218
H	-2.62021	3.18339	0.98841
H	-1.90556	2.26474	-3.15139
H	-3.3114	3.31865	-1.39458
S	0.39691	-1.79861	-0.9455
O	0.23353	-1.56937	-2.39277
O	0.91967	-3.08566	-0.4531
C	-1.16541	-1.46481	-0.14223
C	-1.25428	-1.59689	1.24292
C	-2.24407	-1.01652	-0.89823
C	-2.4393	-1.24075	1.87781
H	-0.40673	-1.96159	1.81276
C	-3.424	-0.66993	-0.24748
H	-2.13923	-0.92219	-1.97154
C	-3.53378	-0.75999	1.14545
H	-2.51622	-1.3297	2.95746
H	-4.26586	-0.30466	-0.82805
C	-4.79064	-0.30933	1.84403
H	-4.77541	0.7767	1.99762
H	-5.68188	-0.54145	1.25408
H	-4.89621	-0.77909	2.82536
H	2.65066	2.36915	0.33165

Zero-point correction = 0.361528 (Hartree/Particle)

Thermal correction to Energy = 0.384429

Thermal correction to Enthalpy = 0.385373

Thermal correction to Gibbs Free Energy = 0.308012

Corrected correction to Gibbs Free Energy = 0.311415

wb97xd/def2tzvp-SMD(MeCN): E = -1398.61834325 hartree

wb97xd/def2tzvp-SMD(DMA): E = -1398.618068 hartree

TS5

C	1.60324	0.09493	0.61337
C	1.10899	1.16448	-0.07363

C	-0.29492	1.65245	-0.03396
C	-0.82182	2.2185	1.1348
C	-1.08136	1.62599	-1.1947
C	-2.11937	2.727	1.14466
H	-0.21842	2.23441	2.03421
C	-2.38145	2.12452	-1.17857
H	-0.68173	1.1785	-2.09915
C	-2.90339	2.67763	-0.00823
H	-2.51839	3.15964	2.05686
H	-2.98721	2.07928	-2.0784
H	-3.916	3.06905	0.00409
C	3.03618	-0.38769	0.57625
H	3.65071	0.28959	1.17901
H	3.07191	-1.37031	1.06563
C	3.62976	-0.50434	-0.79469
C	5.10234	-0.34179	-0.94643
H	5.38641	-0.21081	-1.99407
H	5.46081	0.52371	-0.38212
H	5.6386	-1.22731	-0.56615
C	2.8003	-1.07754	-1.88618
H	2.31162	-2.0074	-1.55711
H	1.98371	-0.39817	-2.17957
H	3.39308	-1.29246	-2.77806
C	1.99352	1.9205	-0.97211
O	3.21939	1.78395	-1.02084
H	1.47736	2.62521	-1.64882
S	0.50752	-0.95702	1.61531
O	1.19138	-2.25979	1.73096
O	0.11413	-0.22467	2.83278
C	-0.95733	-1.21443	0.61935
C	-2.18665	-0.7592	1.08615
C	-0.84532	-1.87211	-0.60432
C	-3.31543	-0.93781	0.29354
H	-2.23815	-0.25325	2.04167
C	-1.98268	-2.03361	-1.38904
H	0.1155	-2.24647	-0.93798
C	-3.22944	-1.55981	-0.95833
H	-4.27613	-0.57283	0.64444
H	-1.90468	-2.53636	-2.34872
C	-4.44869	-1.68483	-1.83519
H	-4.32769	-2.4732	-2.58256
H	-5.34368	-1.90502	-1.24617
H	-4.63602	-0.74651	-2.3716

Zero-point correction = 0.360416 (Hartree/Particle)

Thermal correction to Energy = 0.383650

Thermal correction to Enthalpy = 0.384594

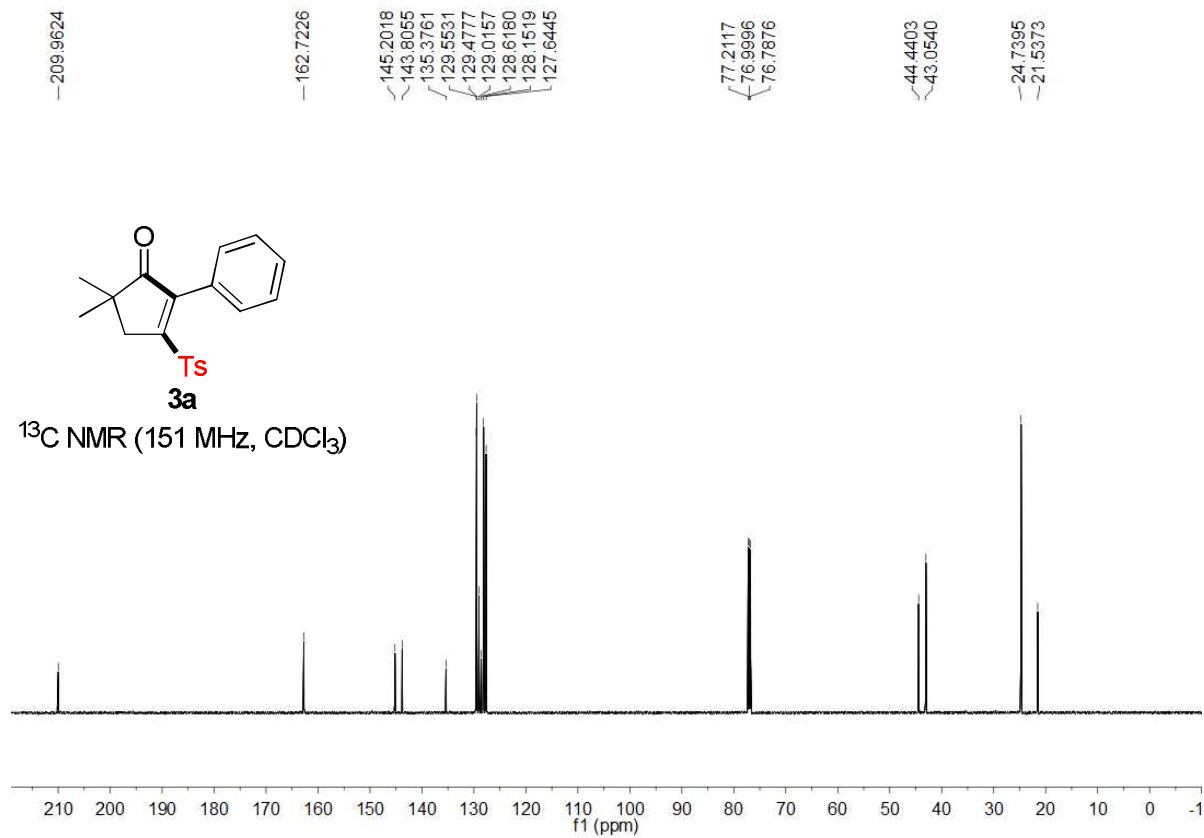
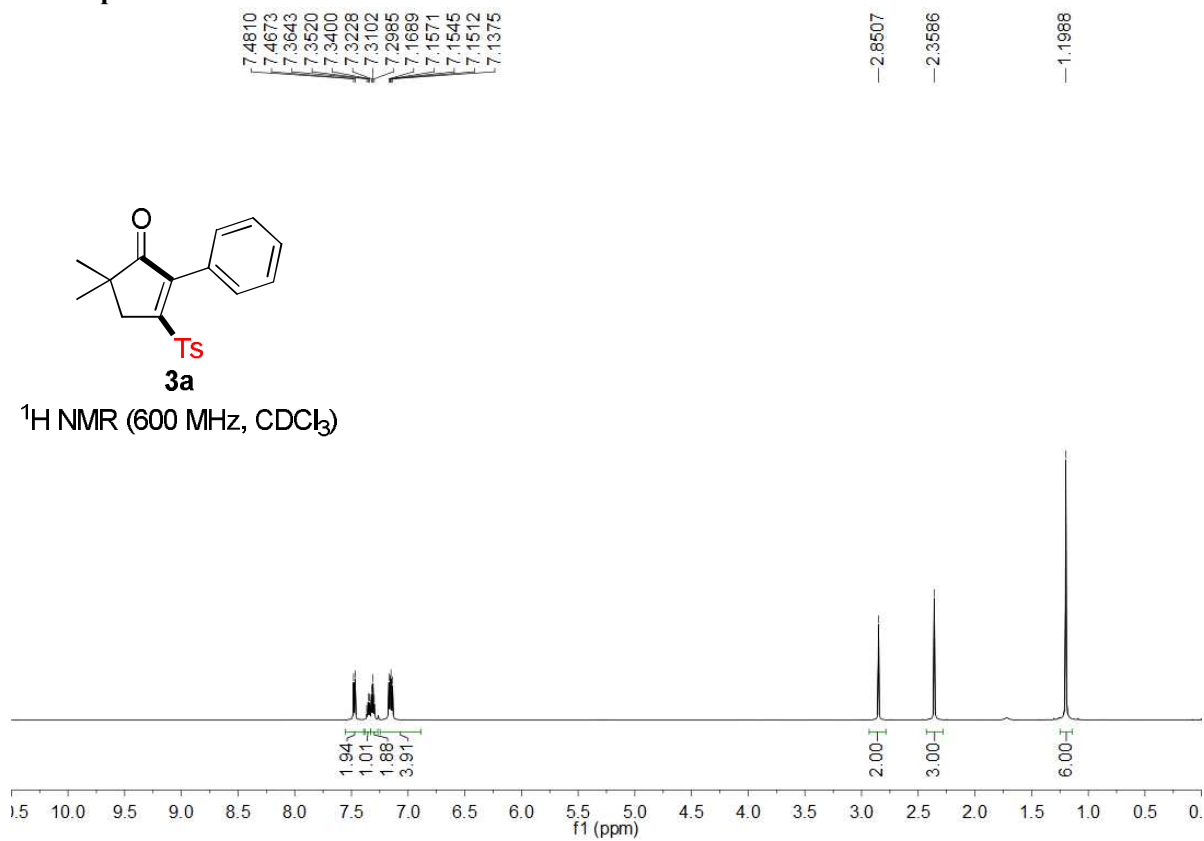
Thermal correction to Gibbs Free Energy = 0.306639

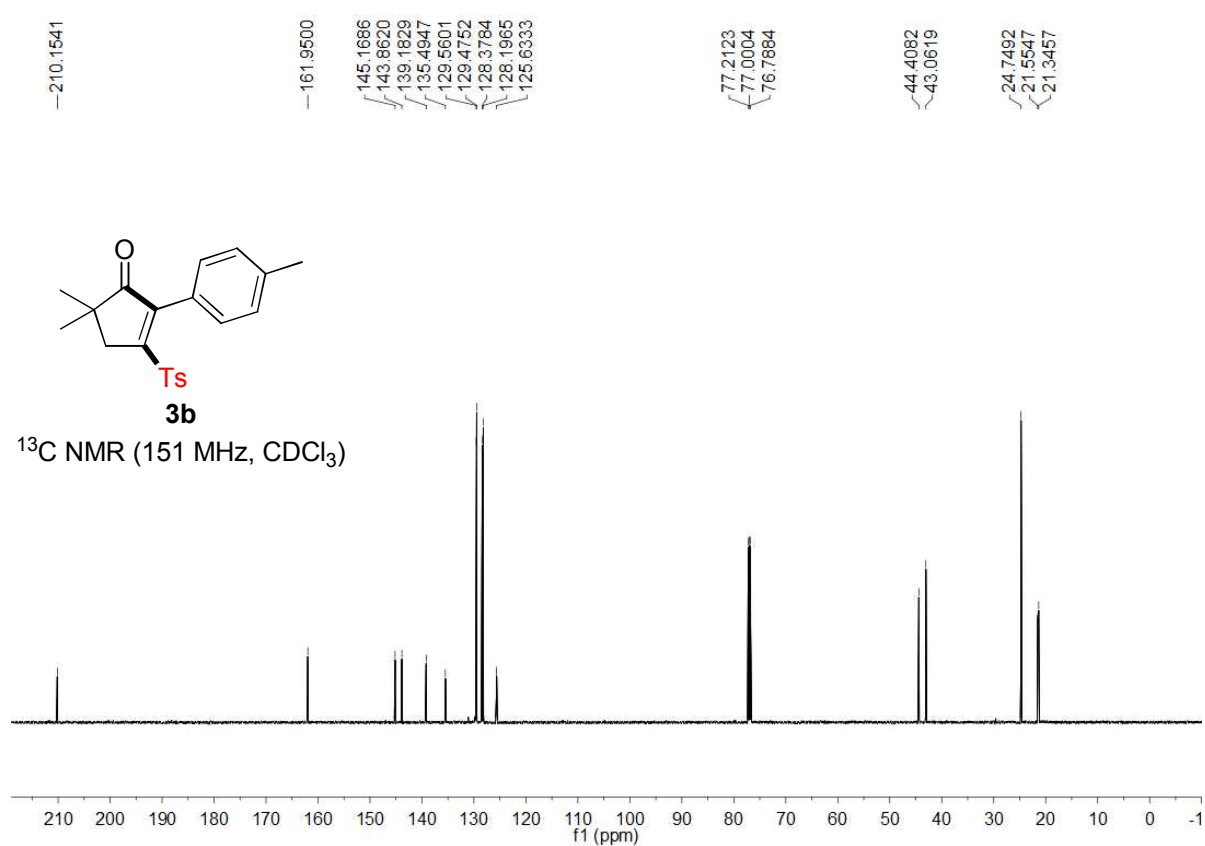
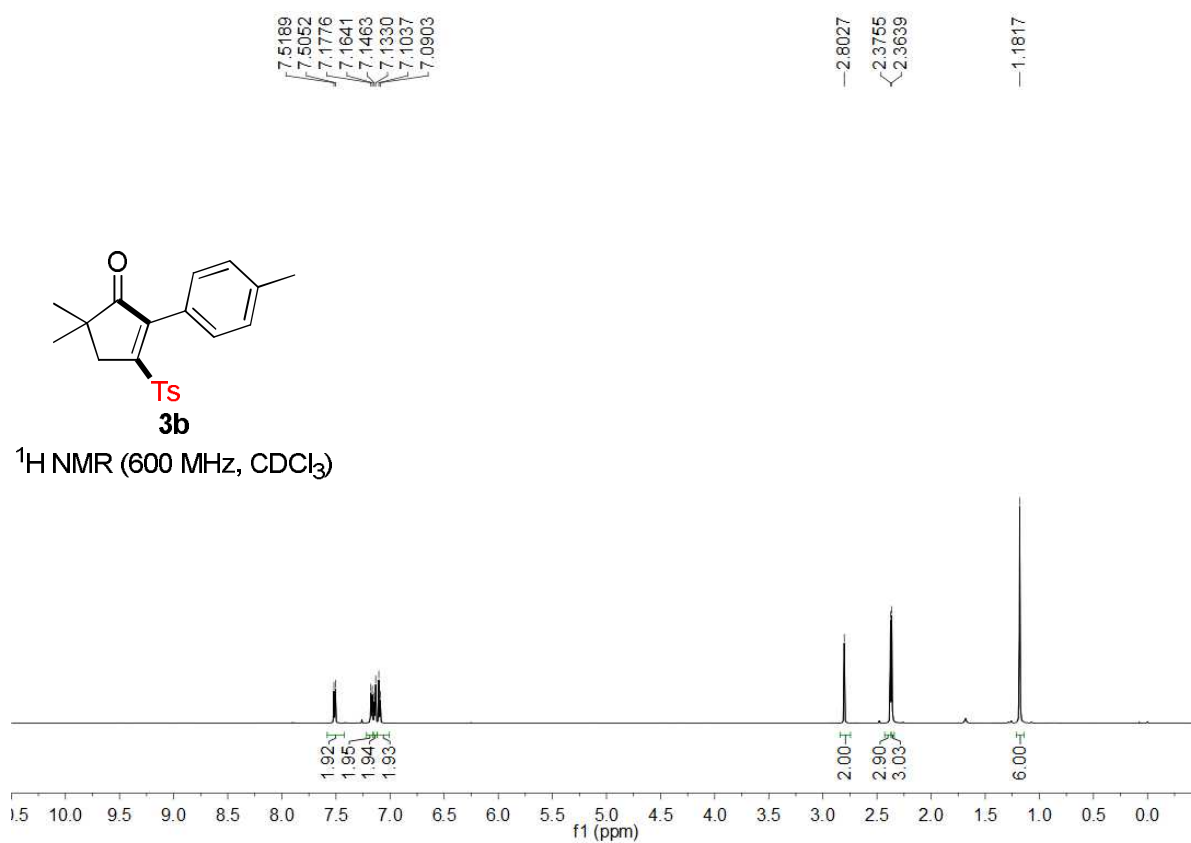
Corrected correction to Gibbs Free Energy = 0.309732

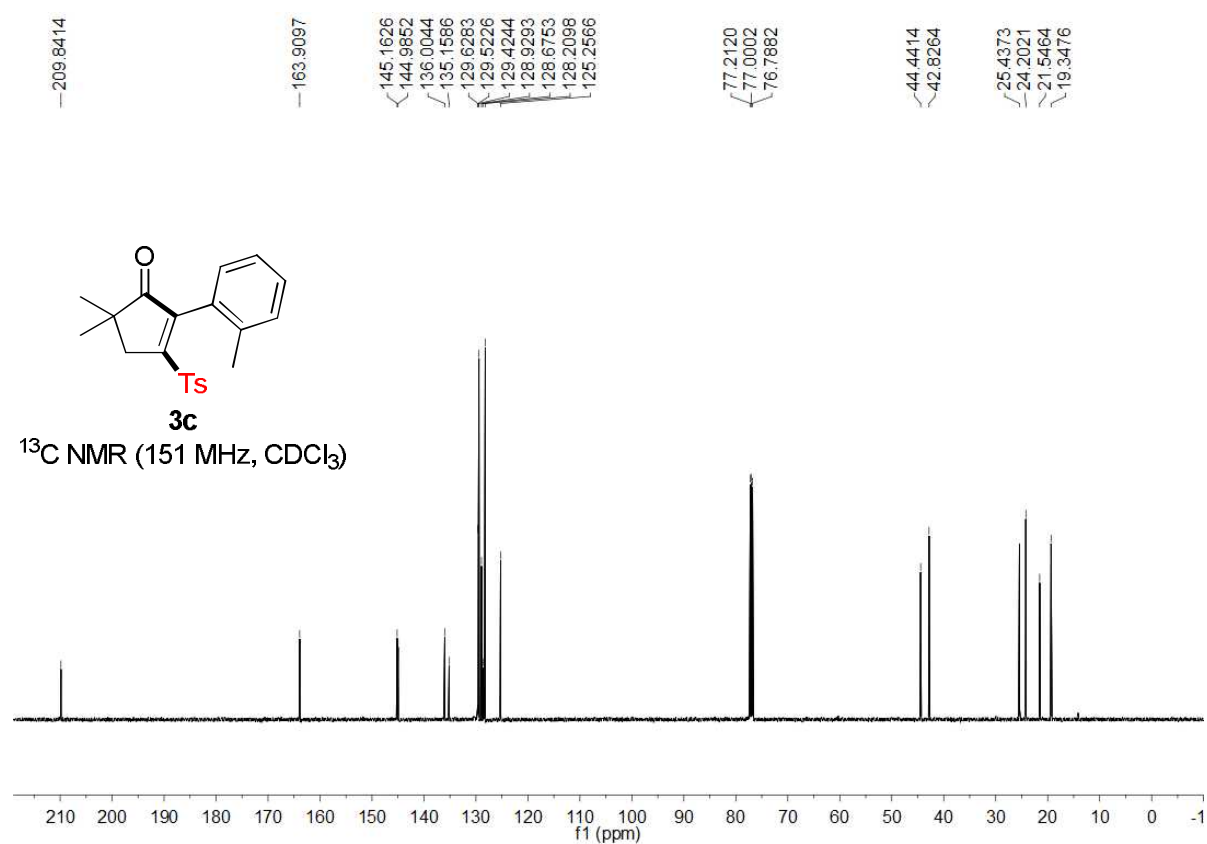
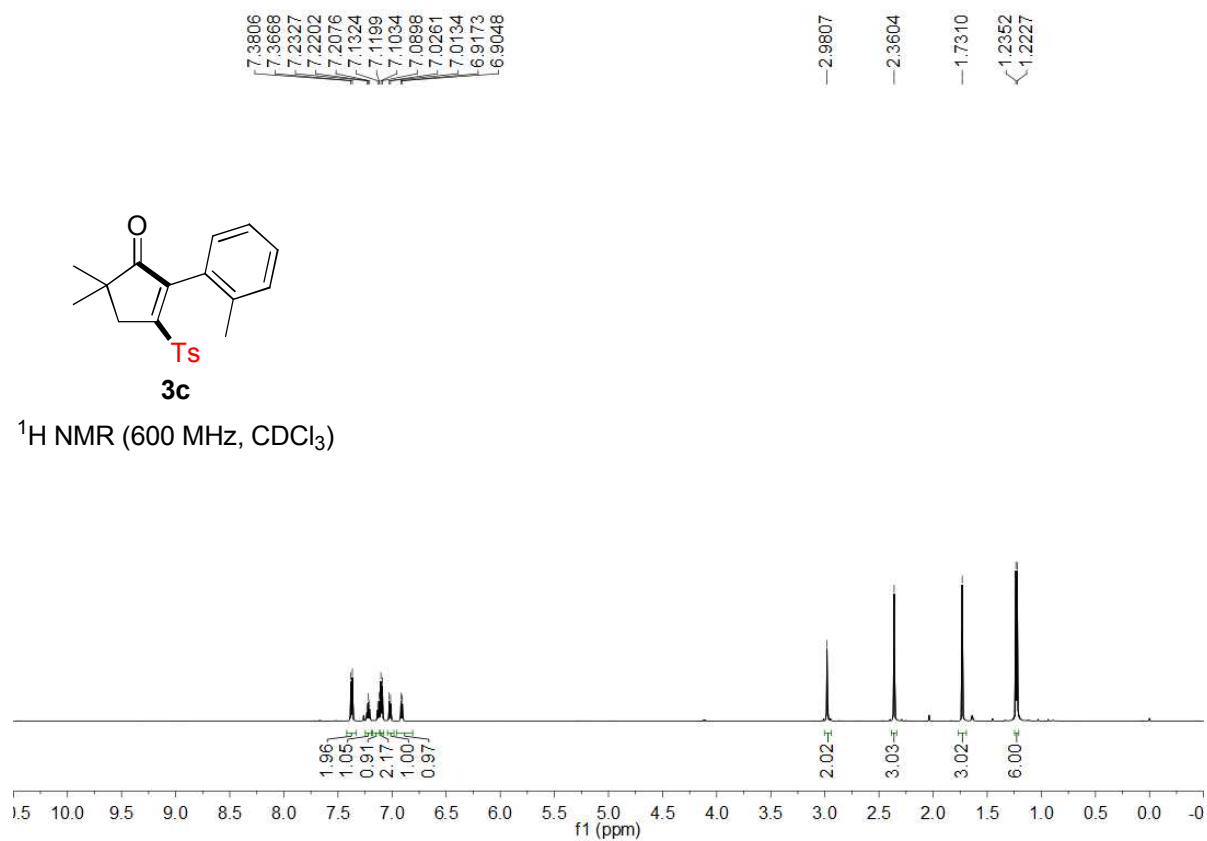
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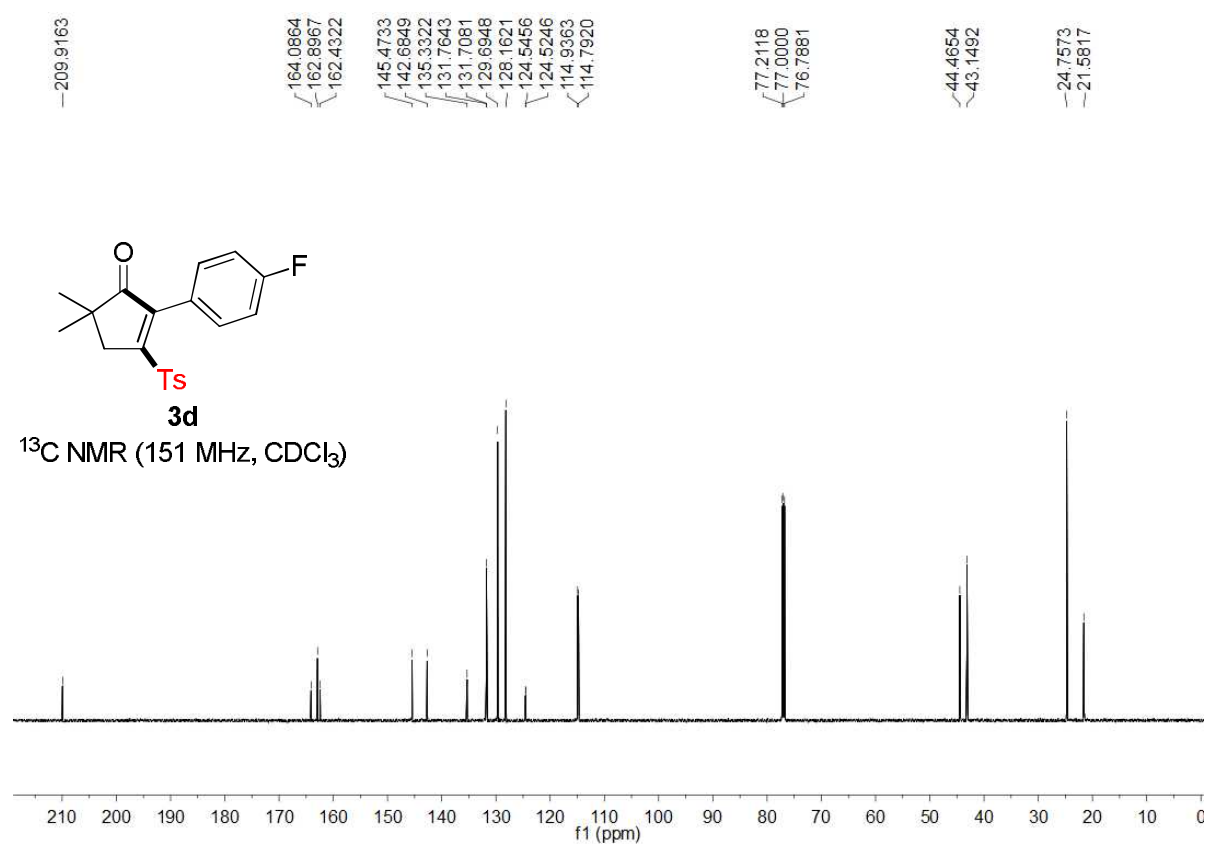
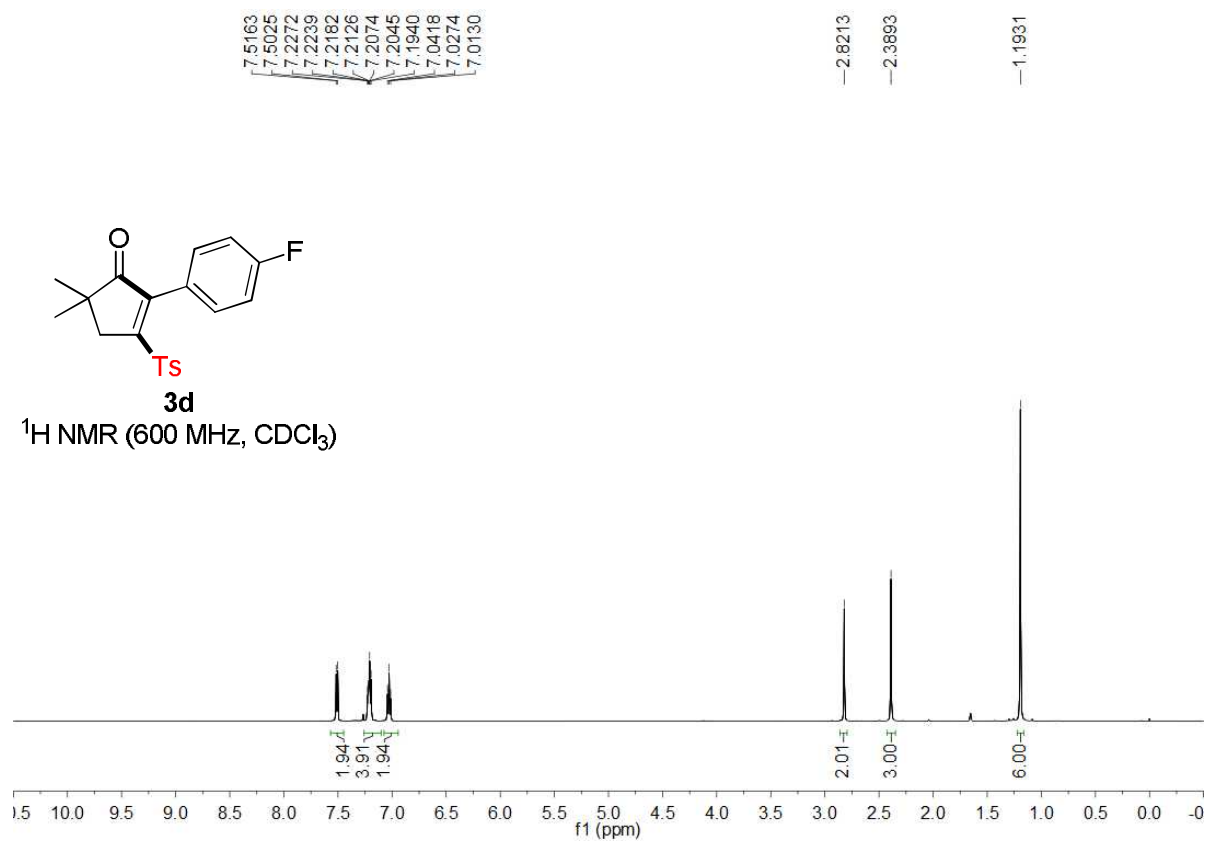
wb97xd/def2tzvp-SMD(DMA): E = -1398.610028 hartree

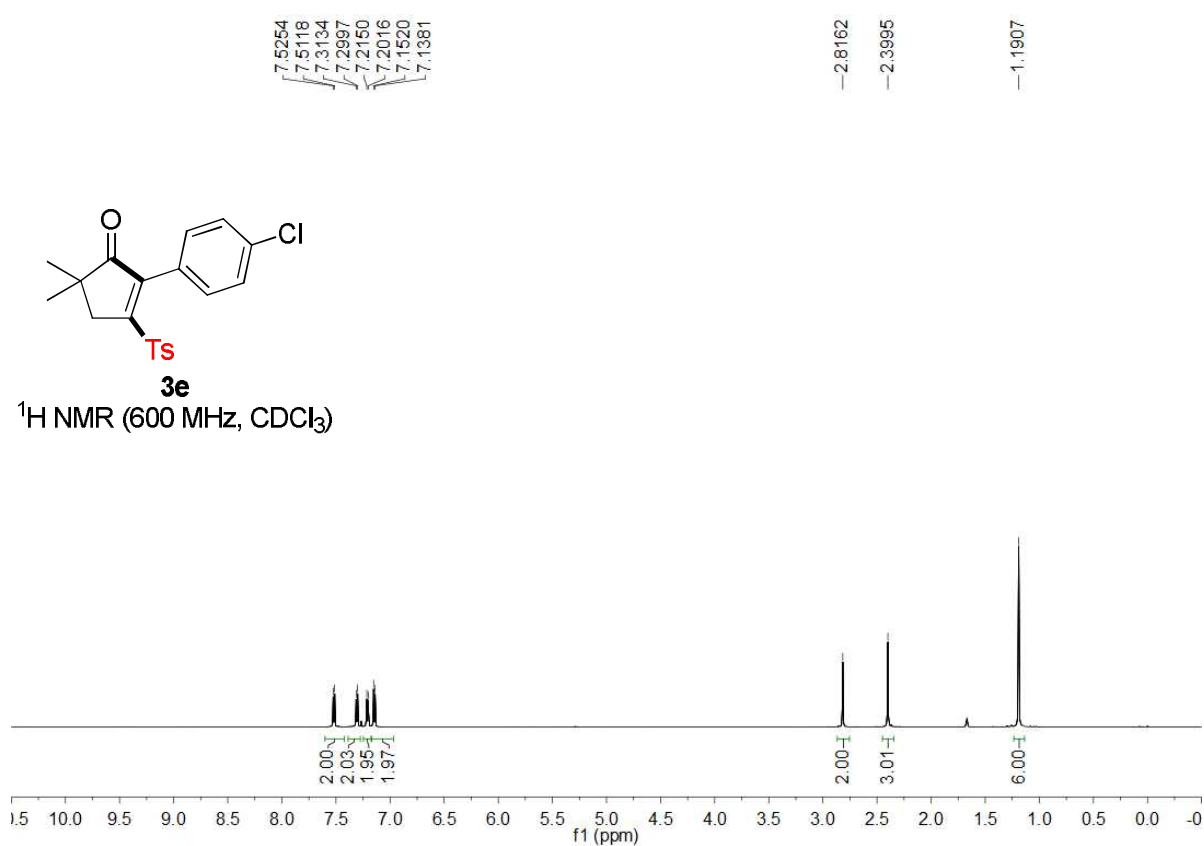
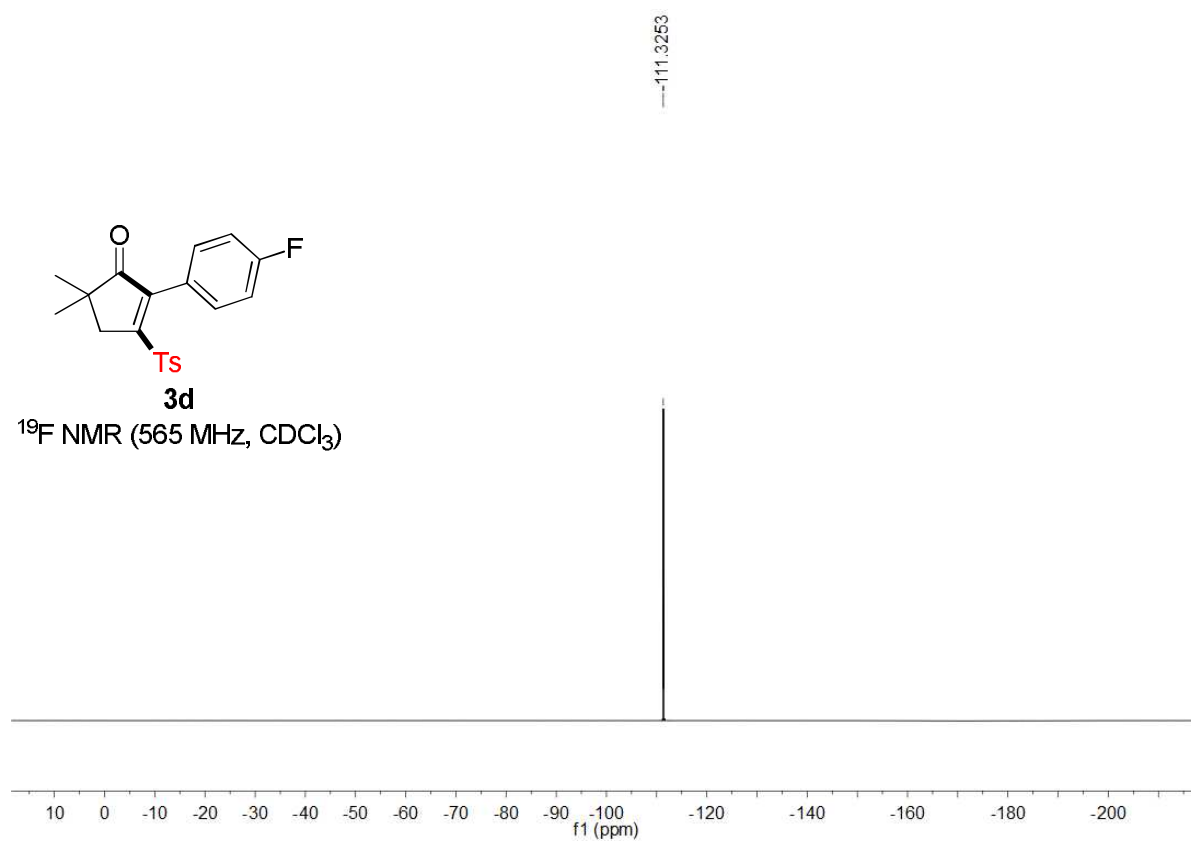
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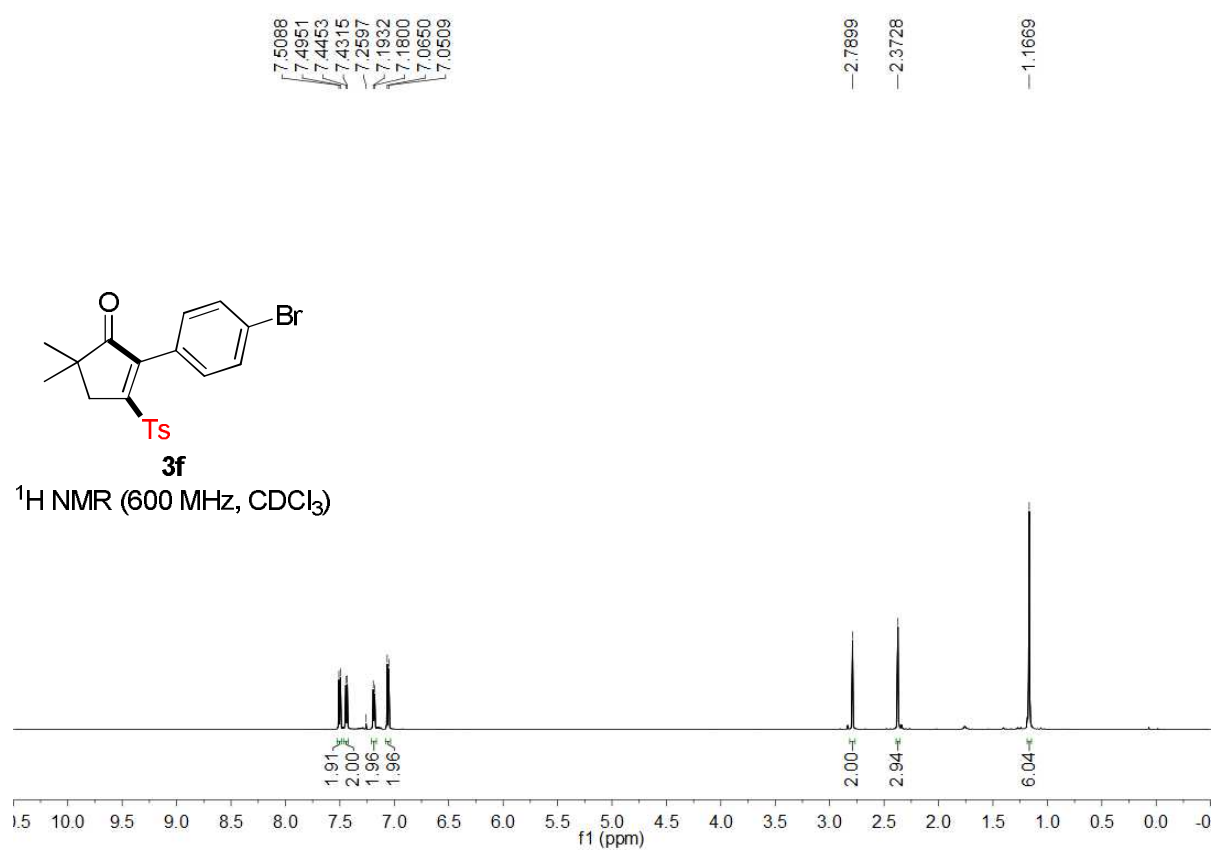
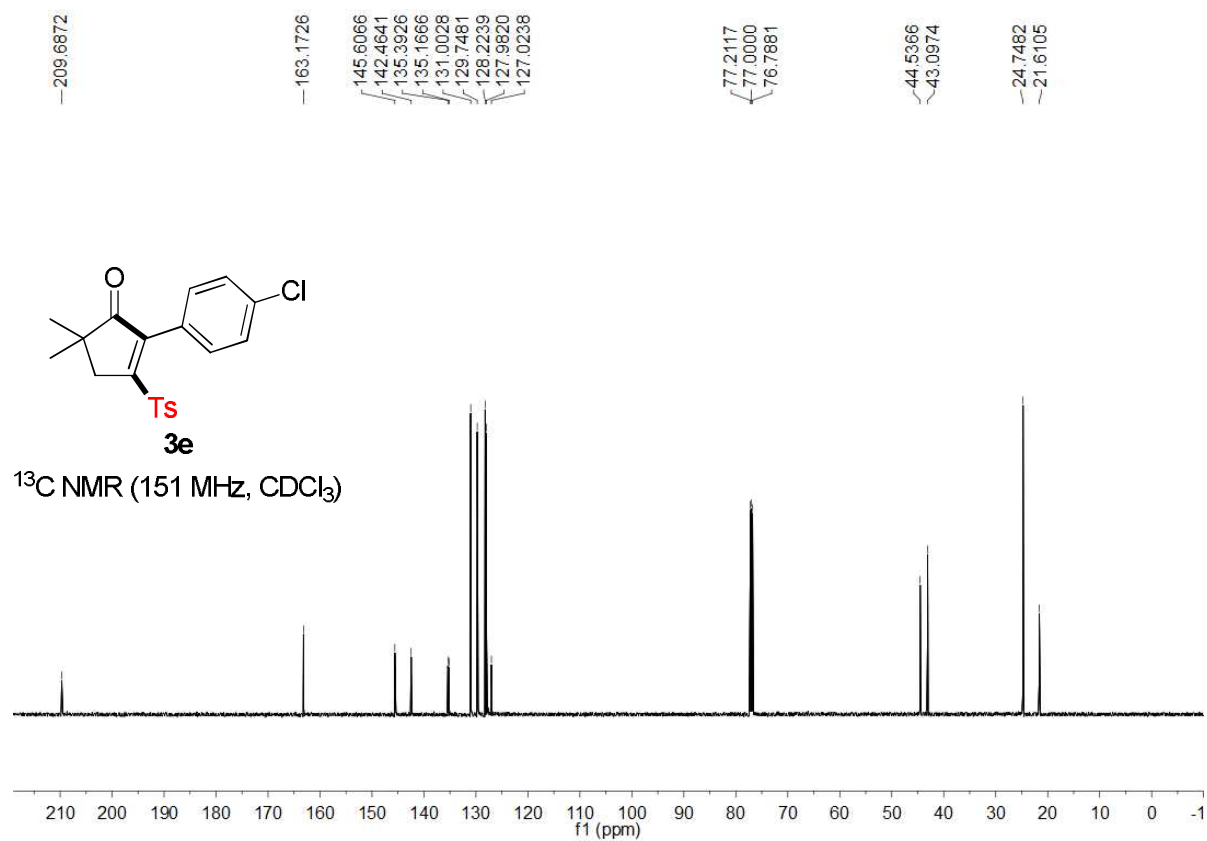


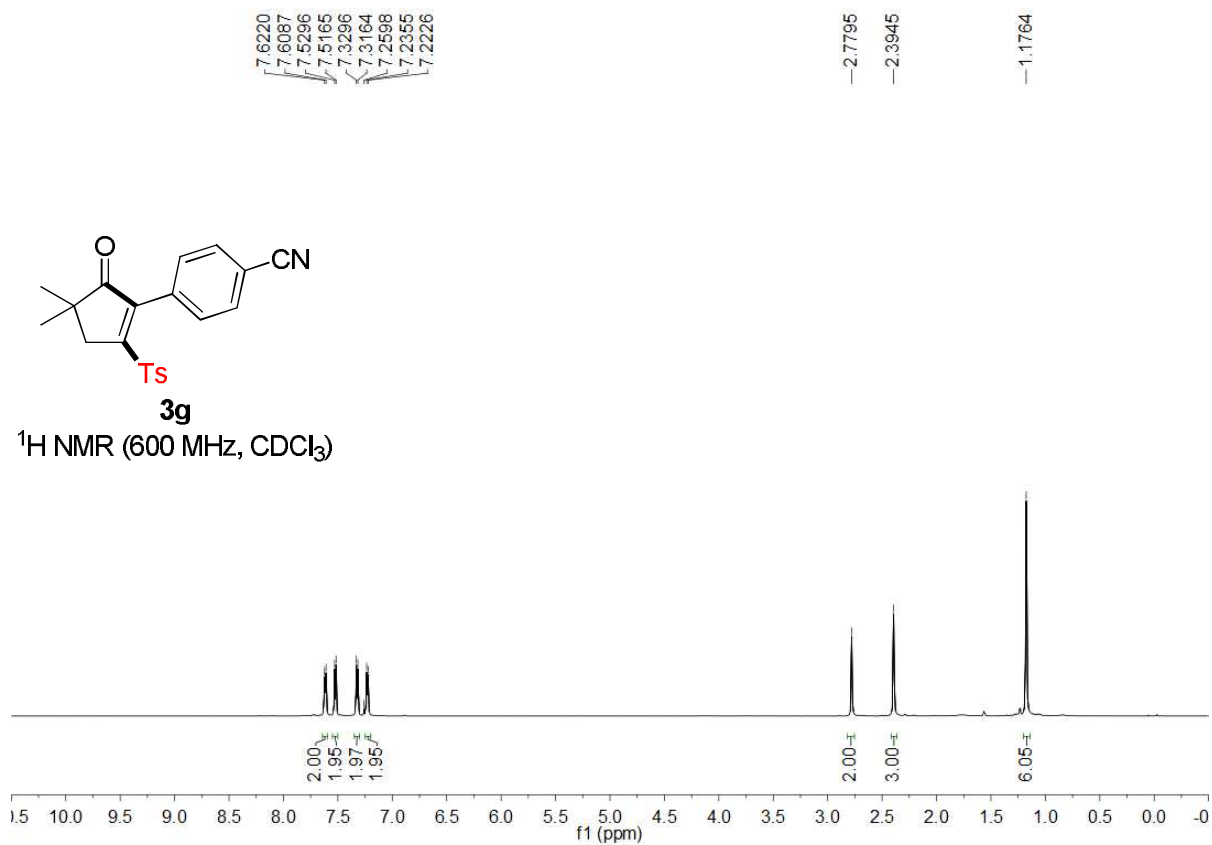
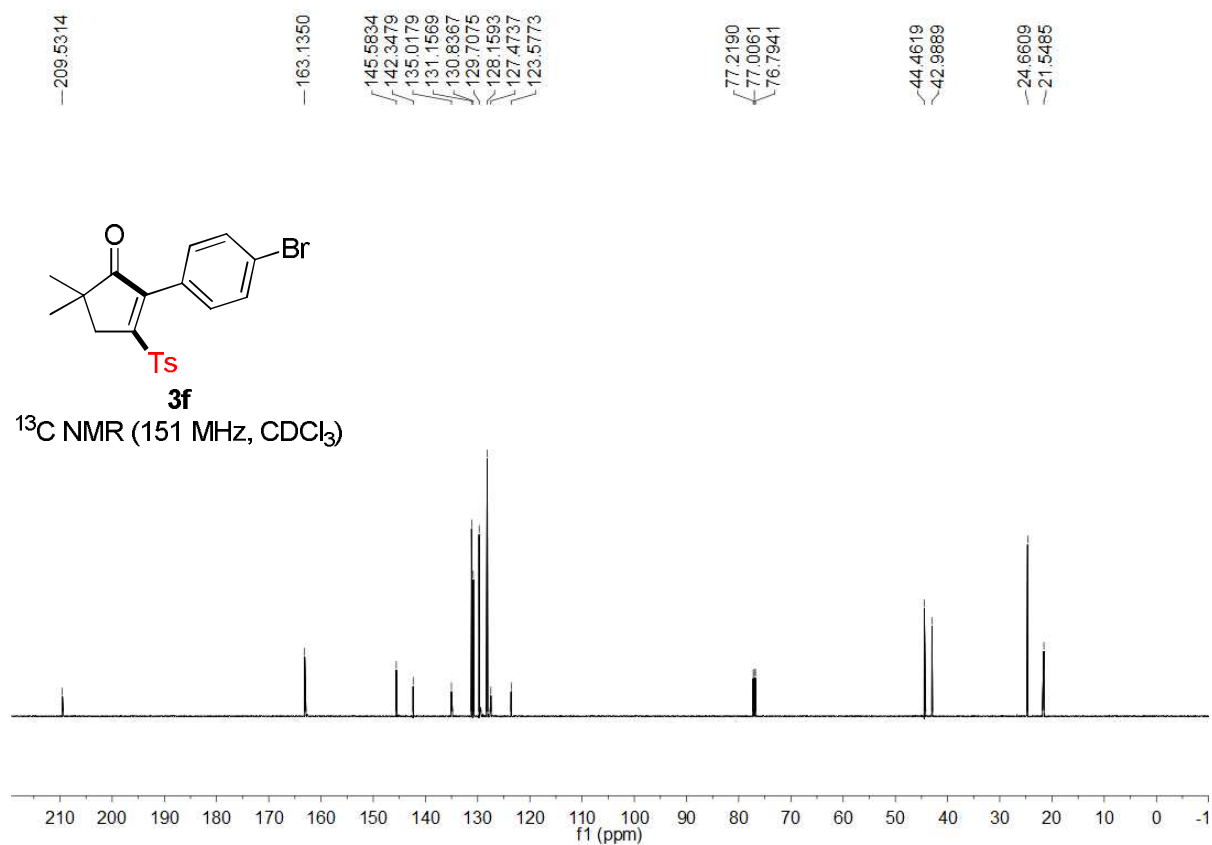


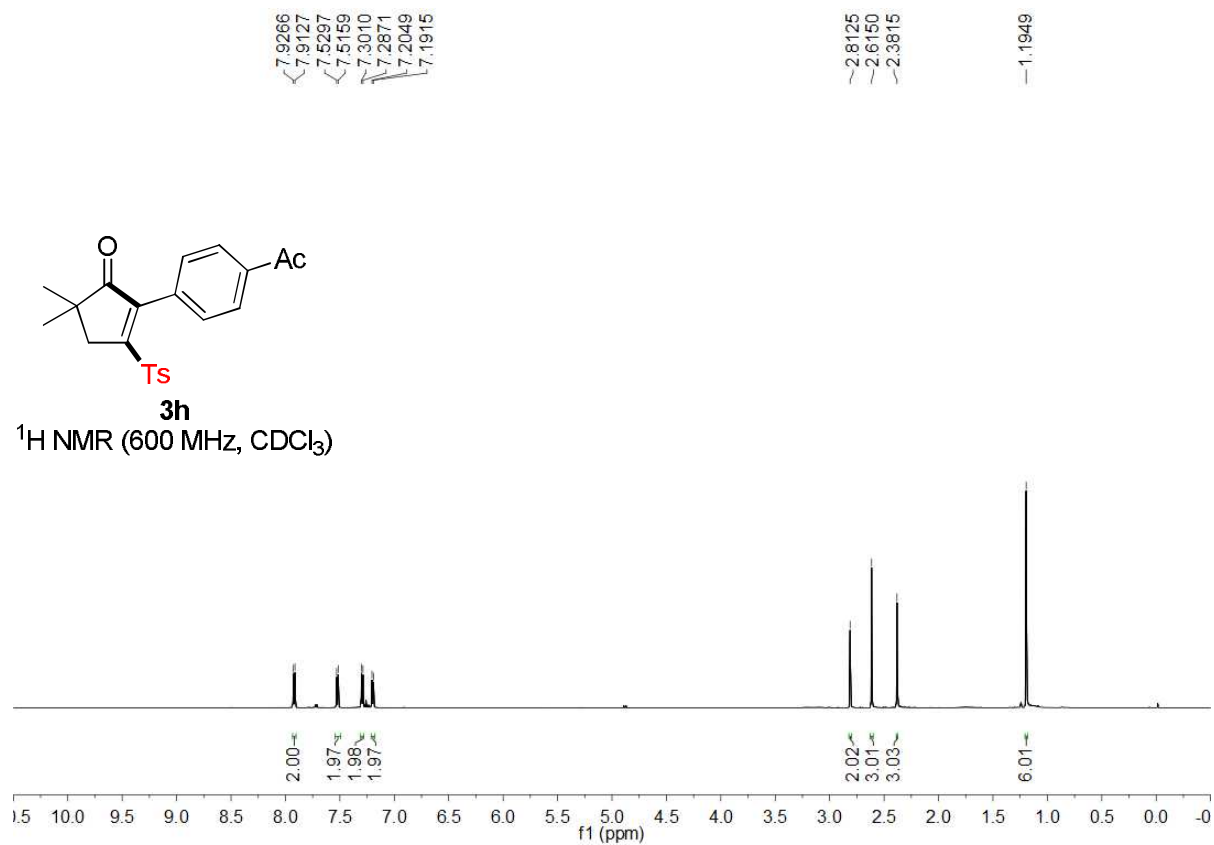
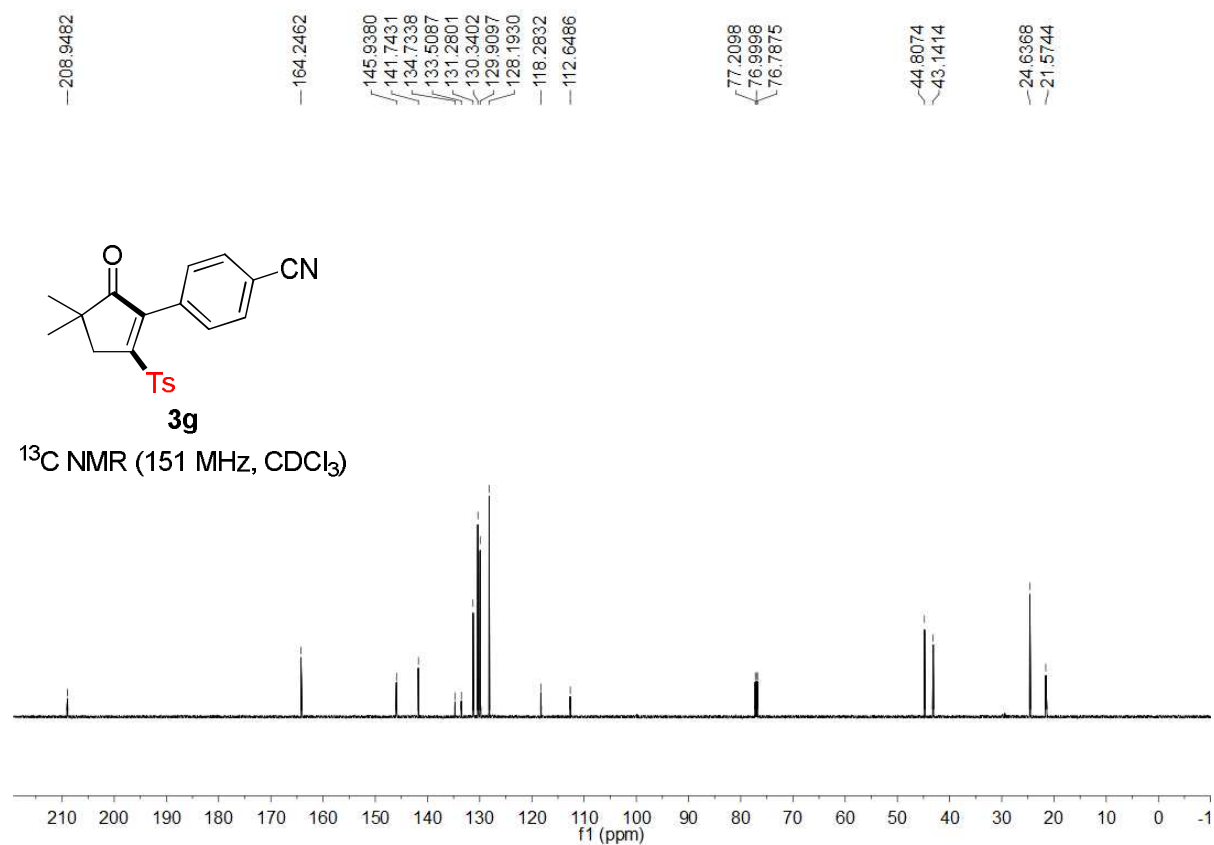


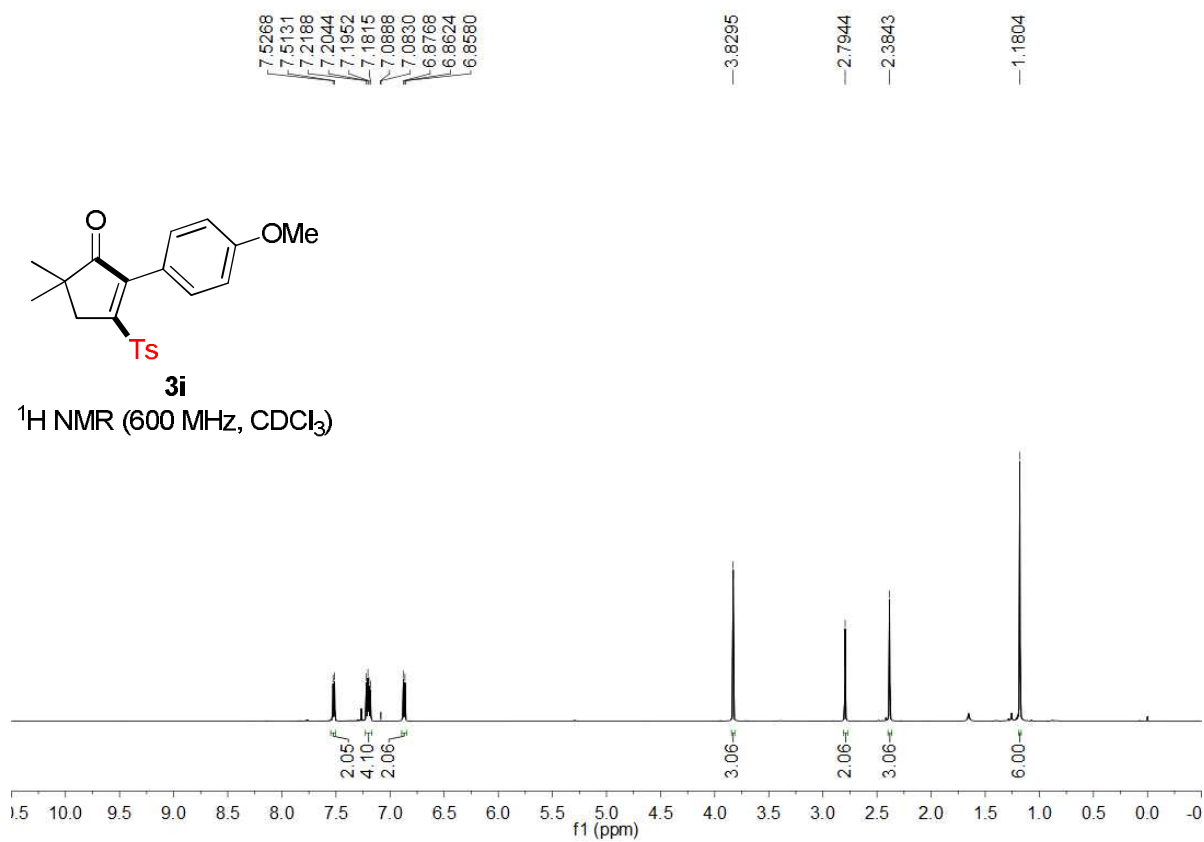
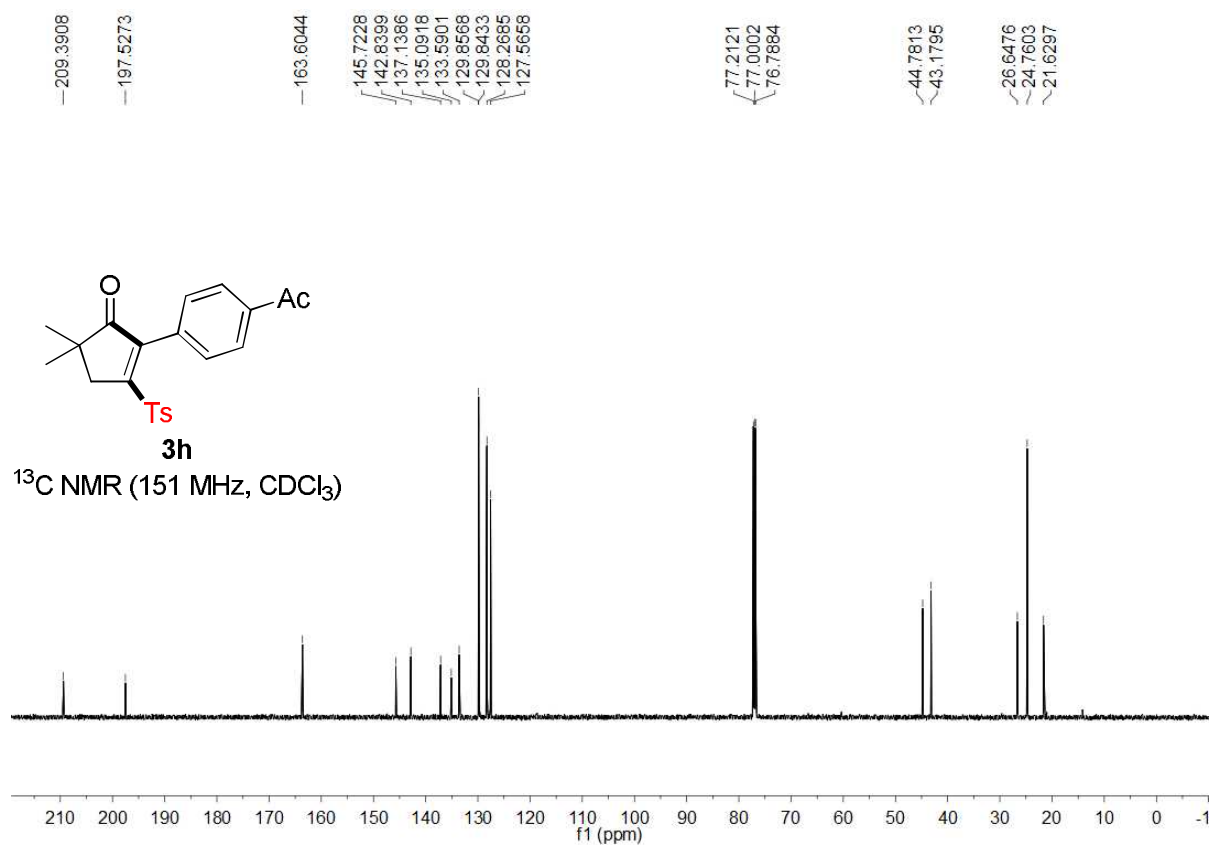


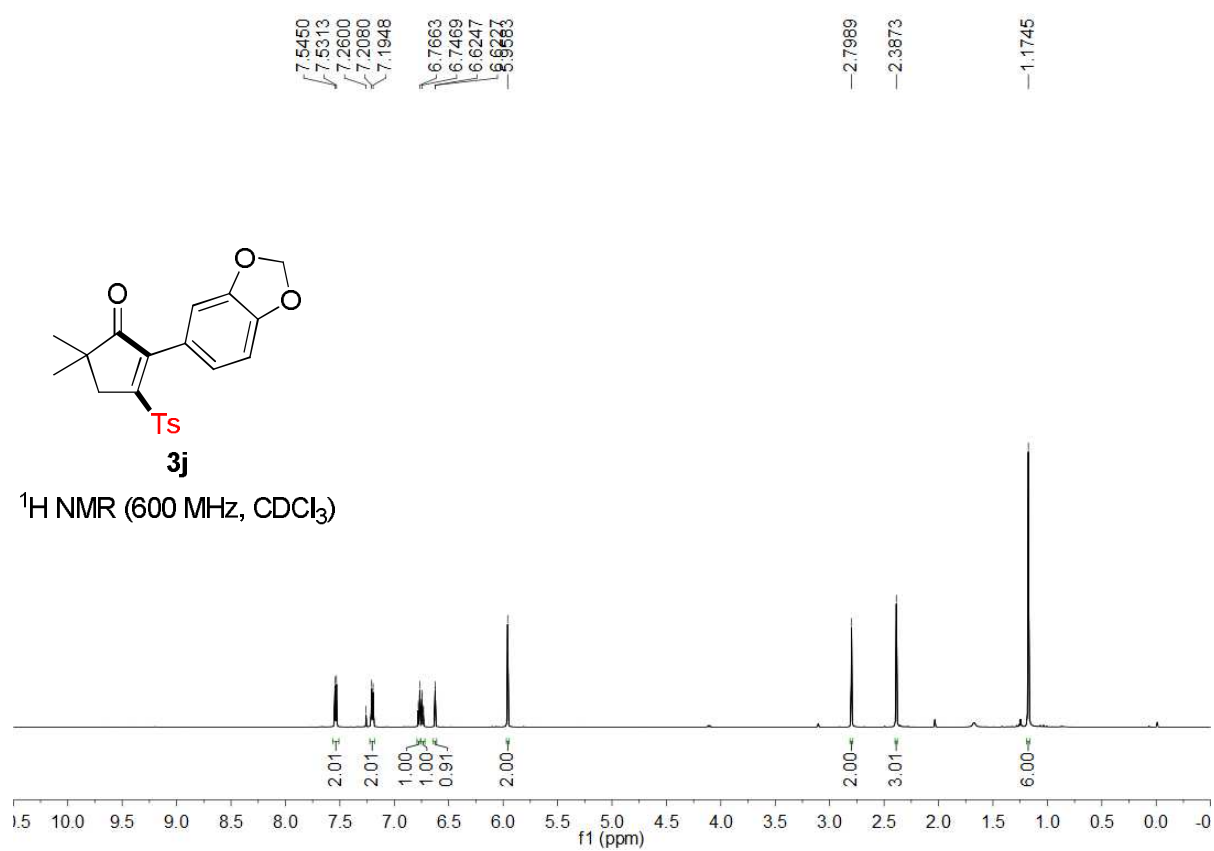
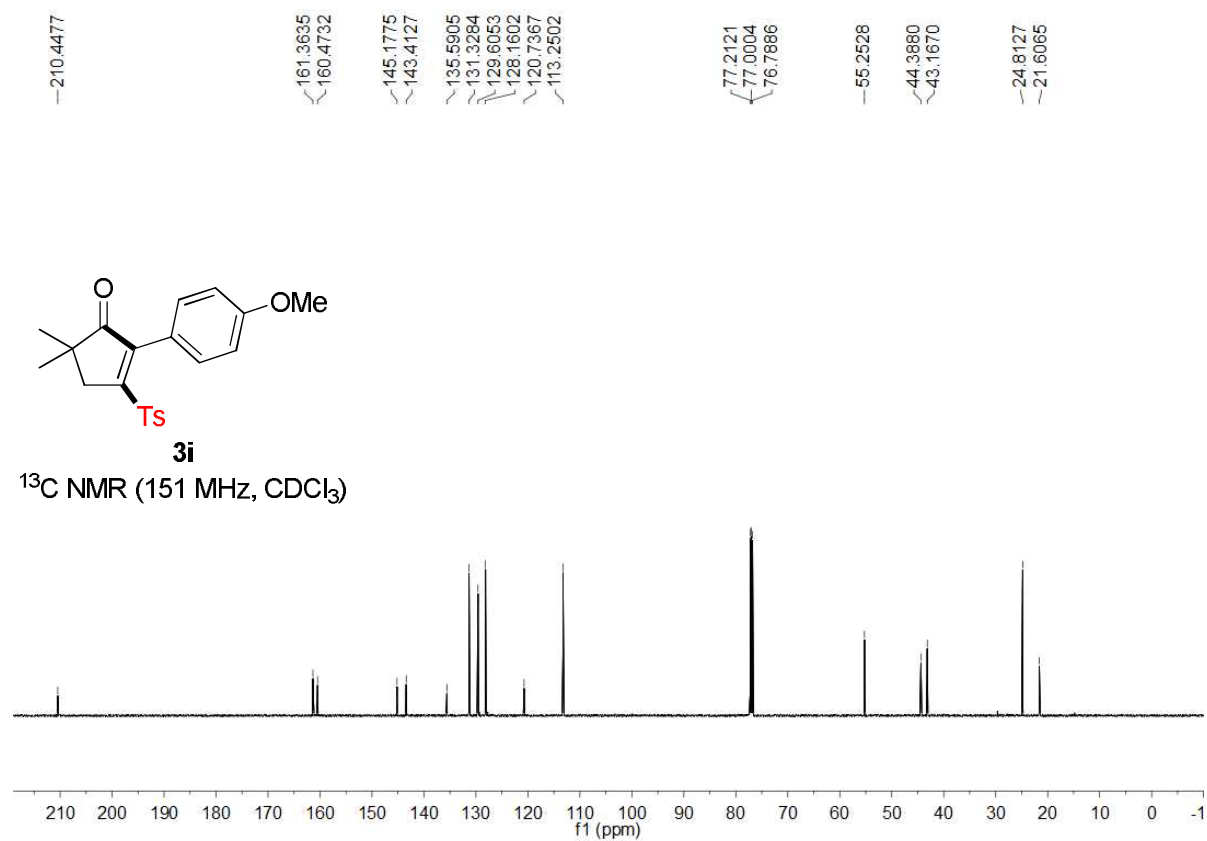


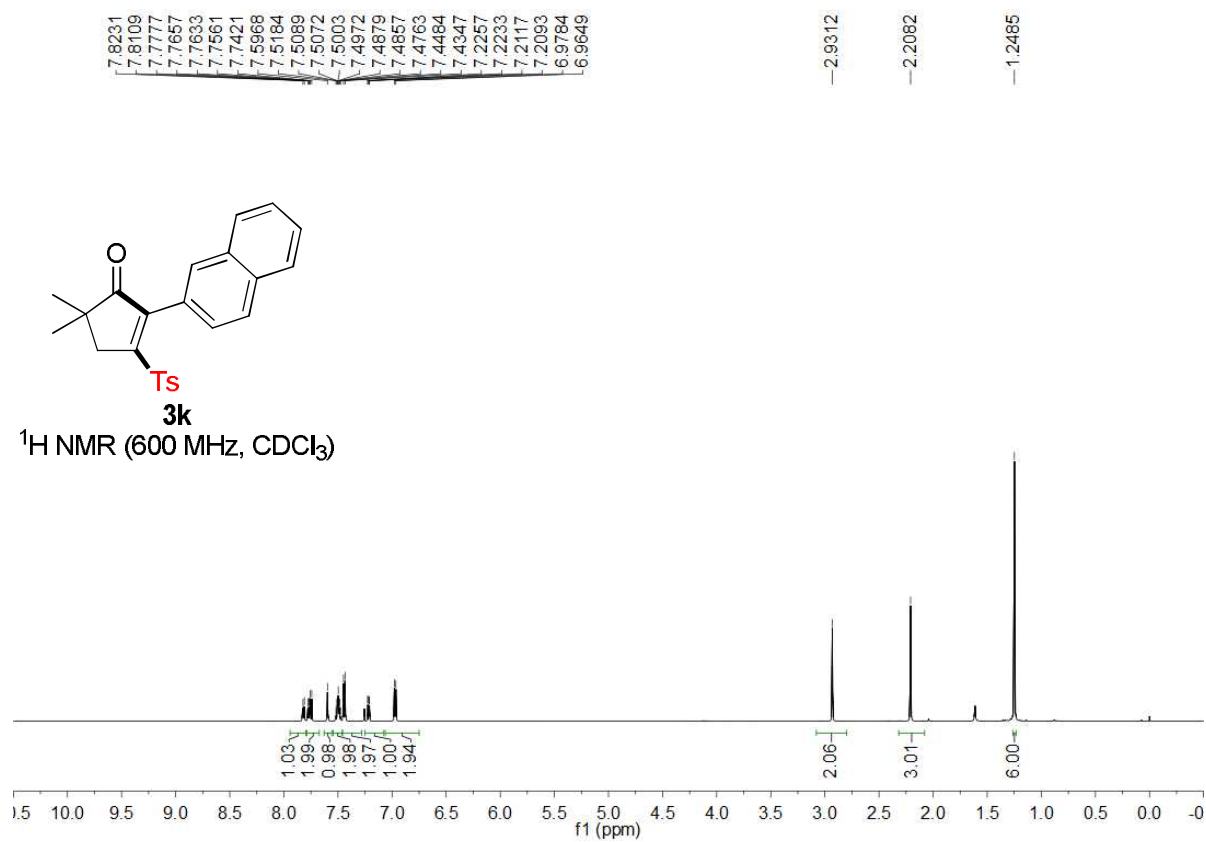
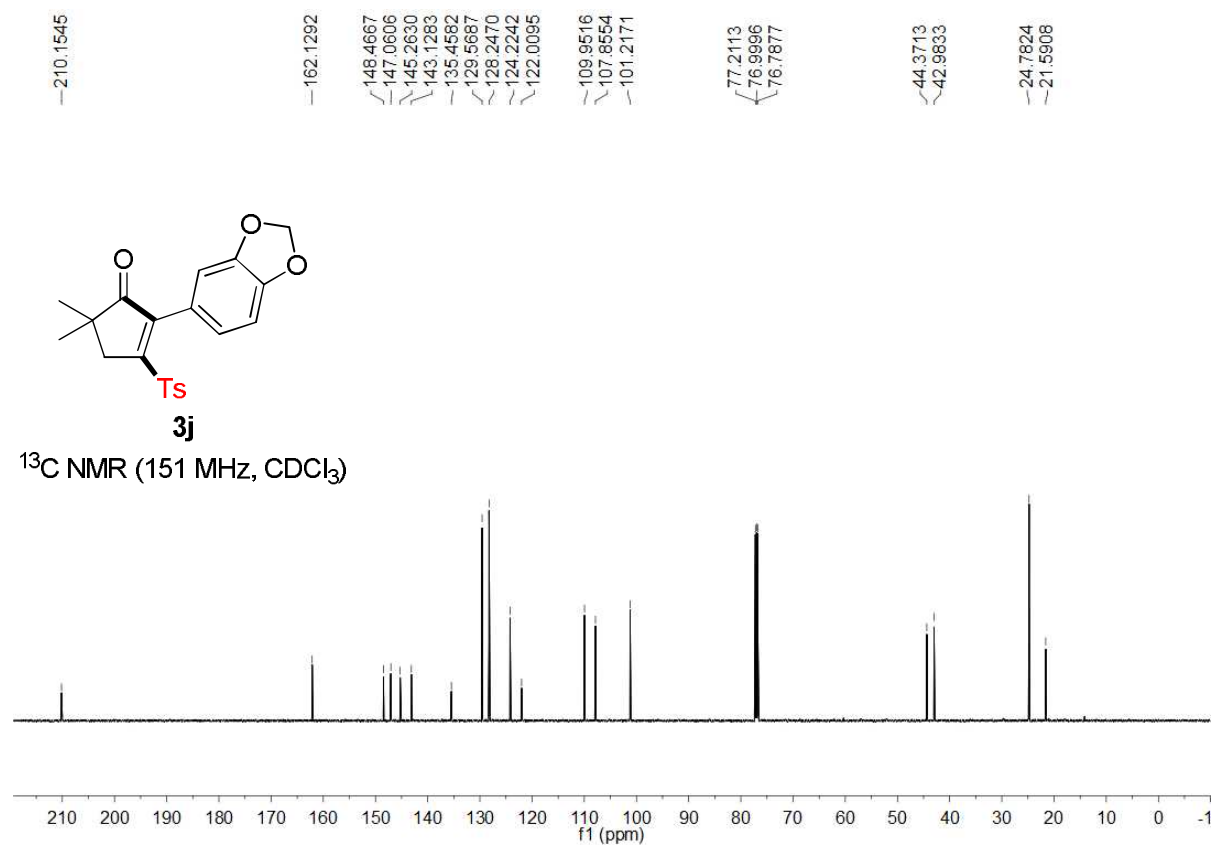


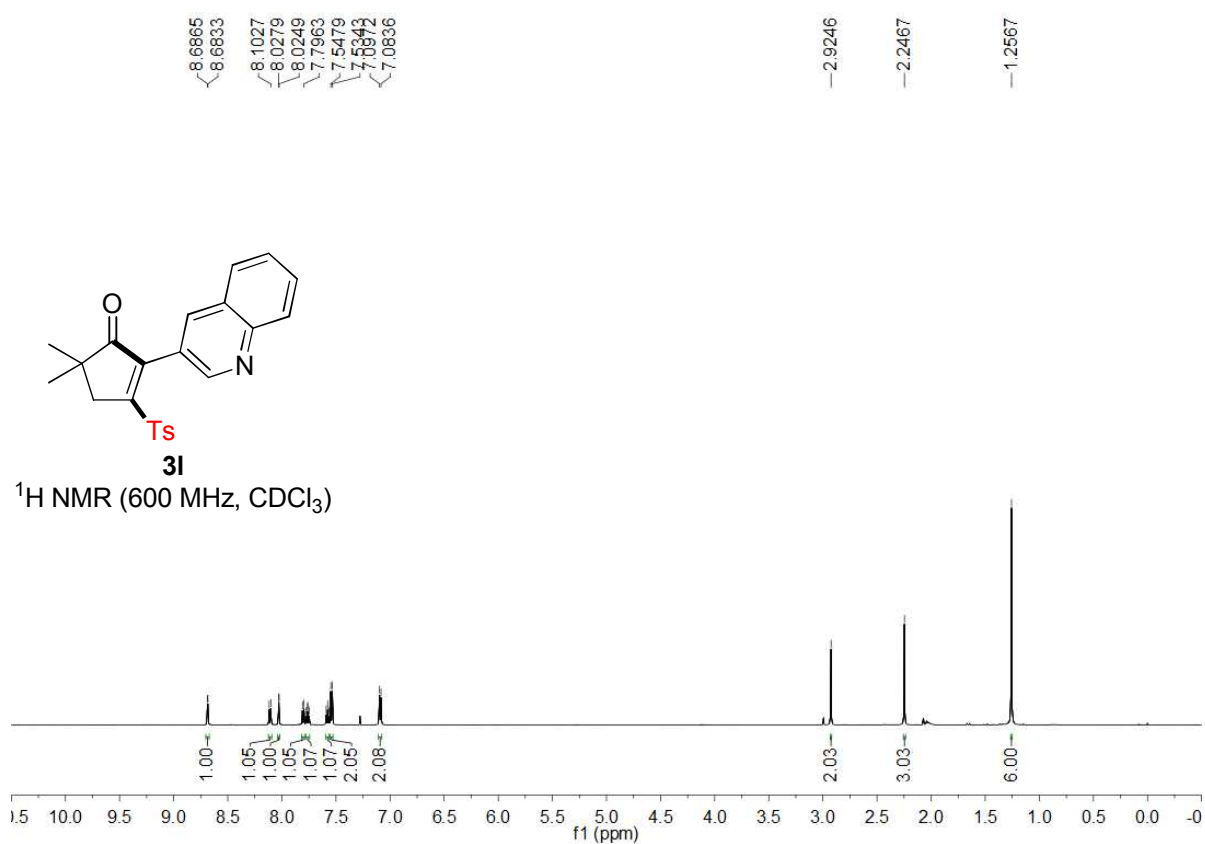
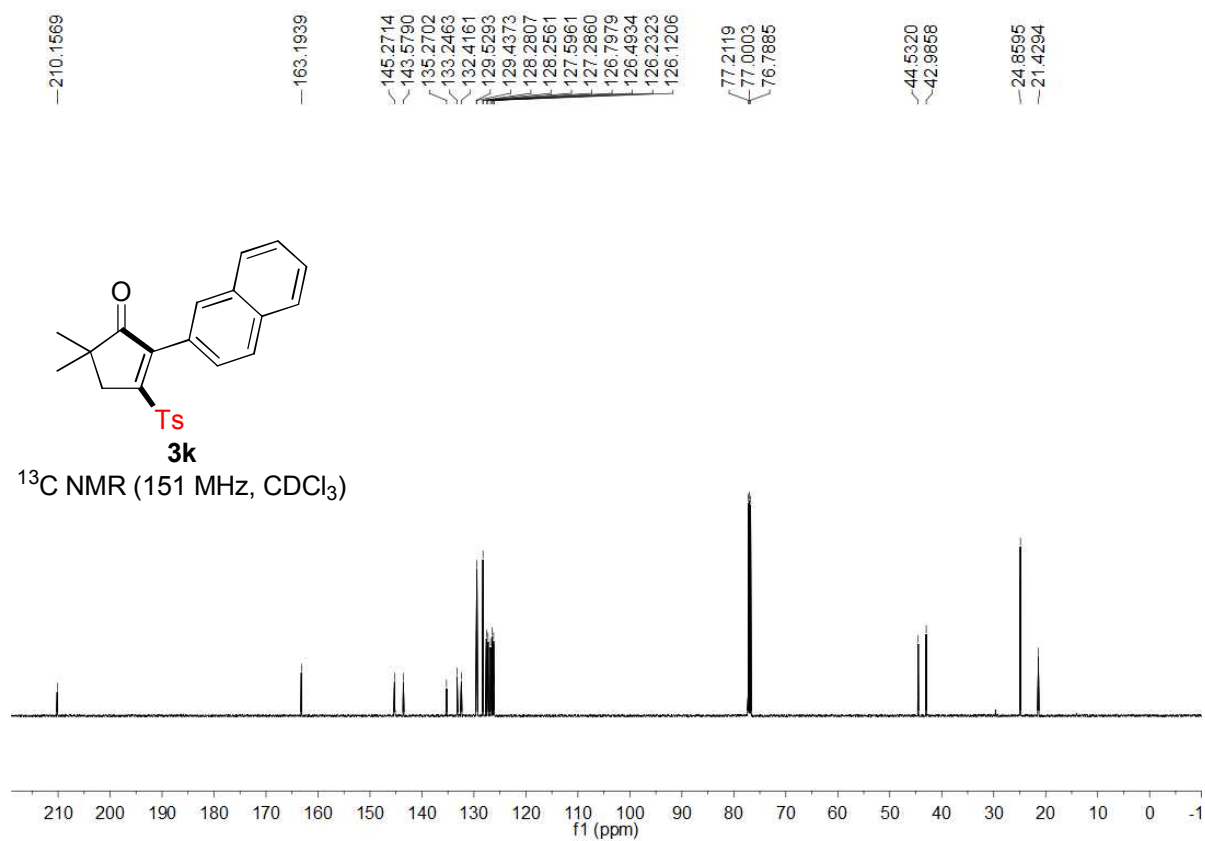


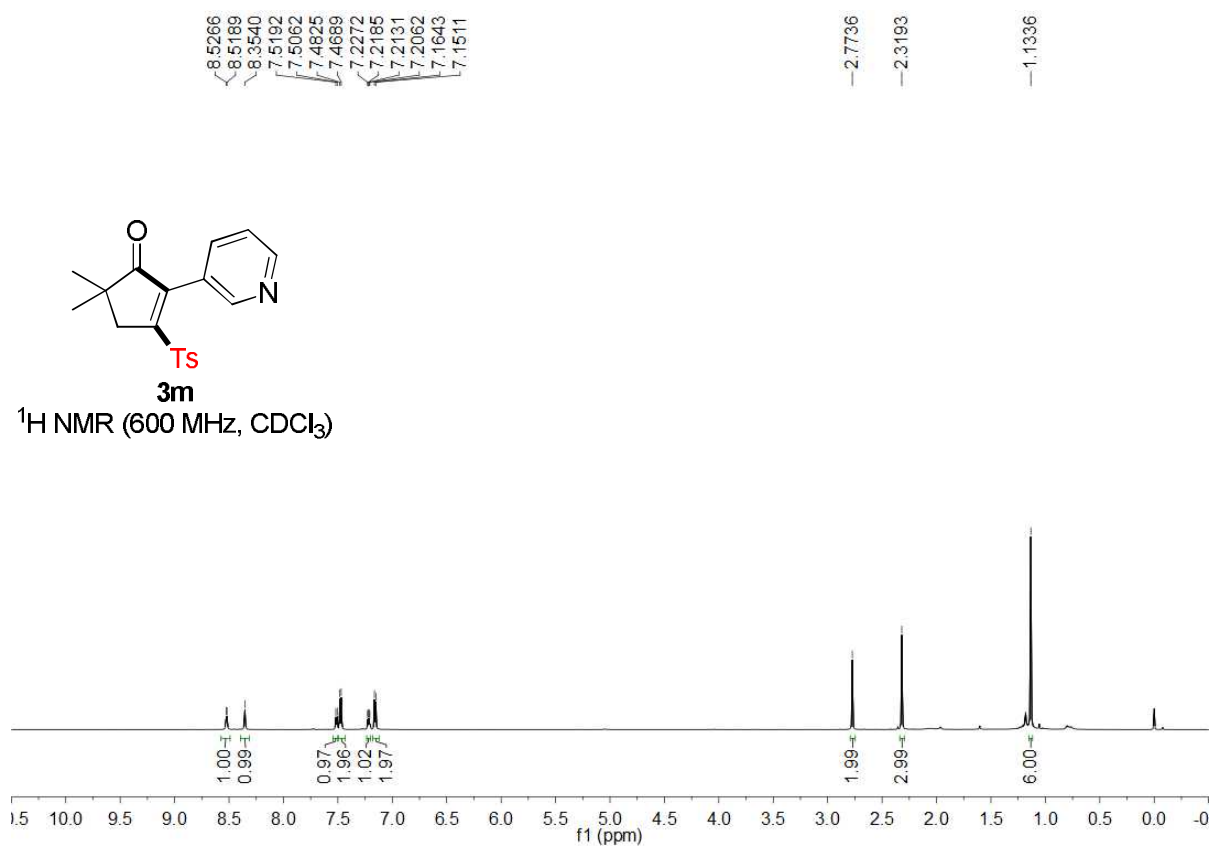
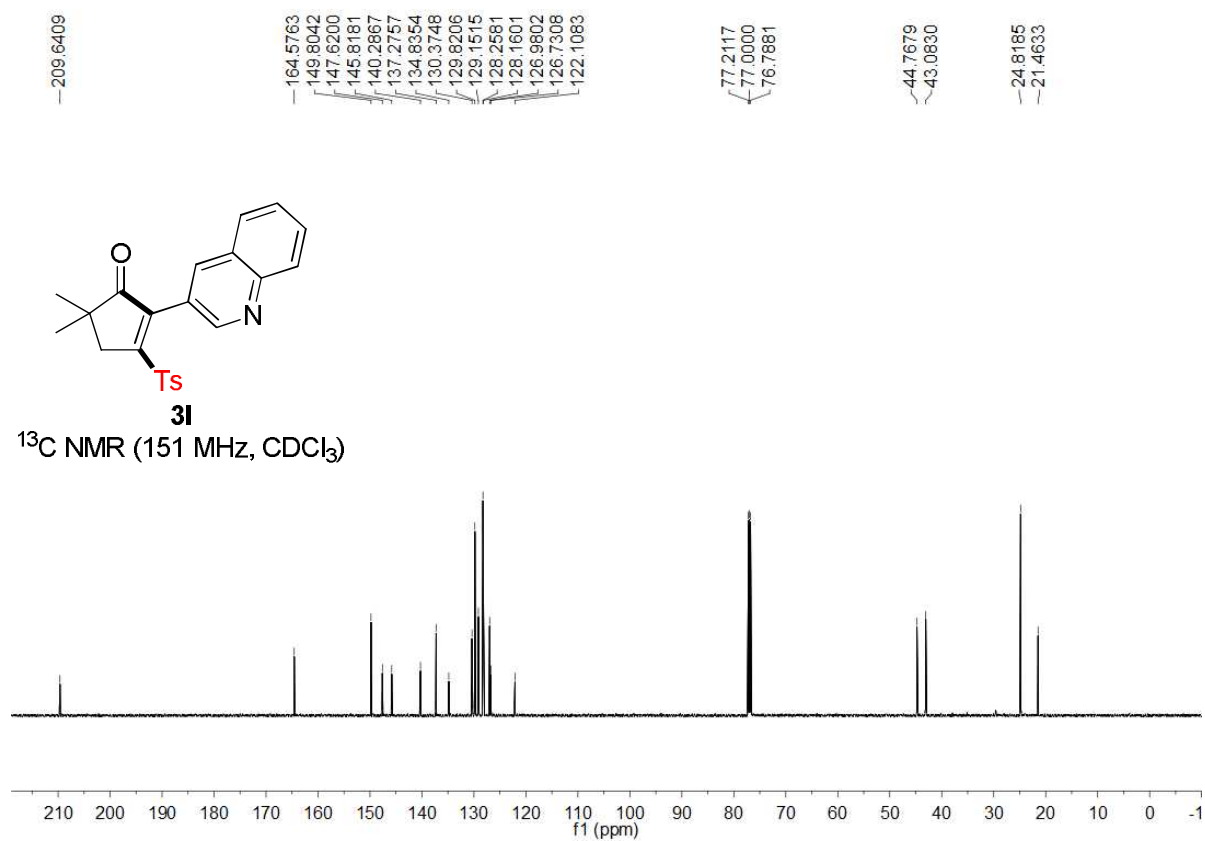


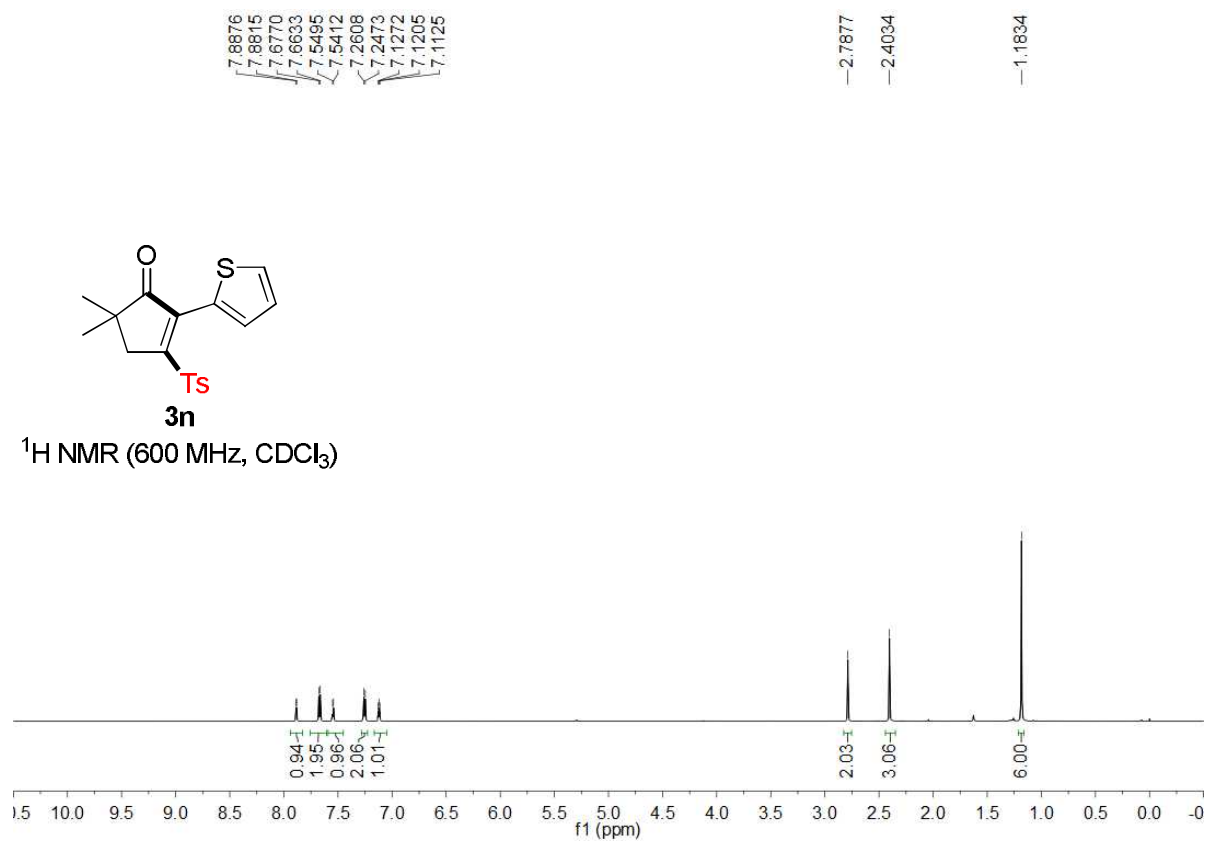
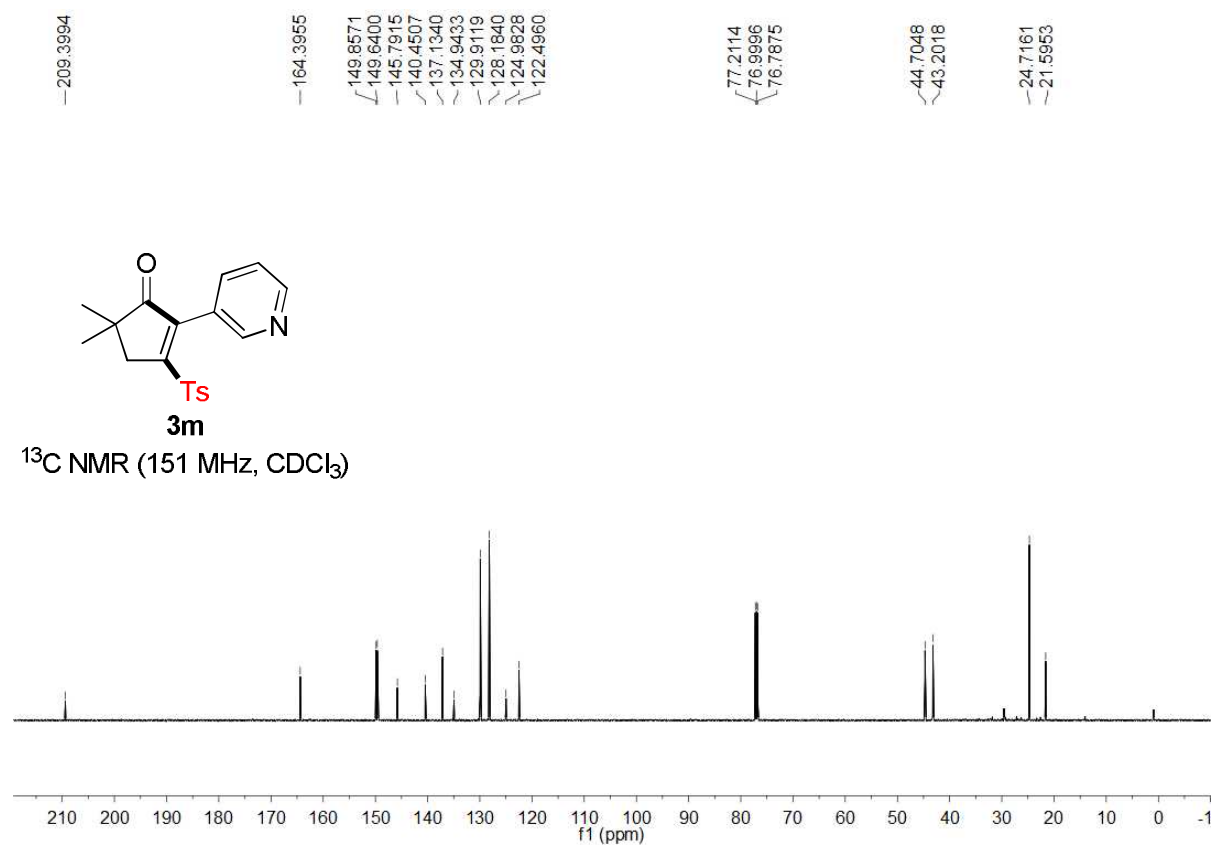


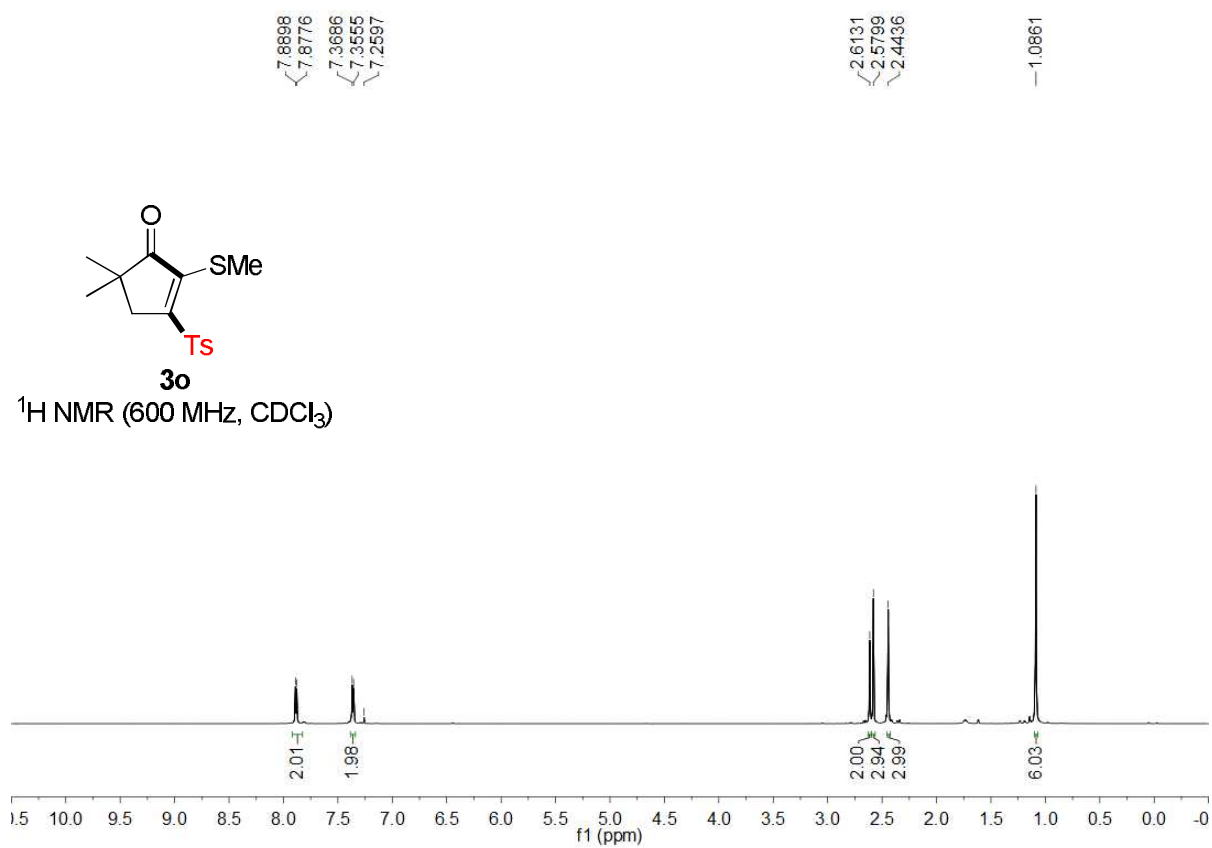
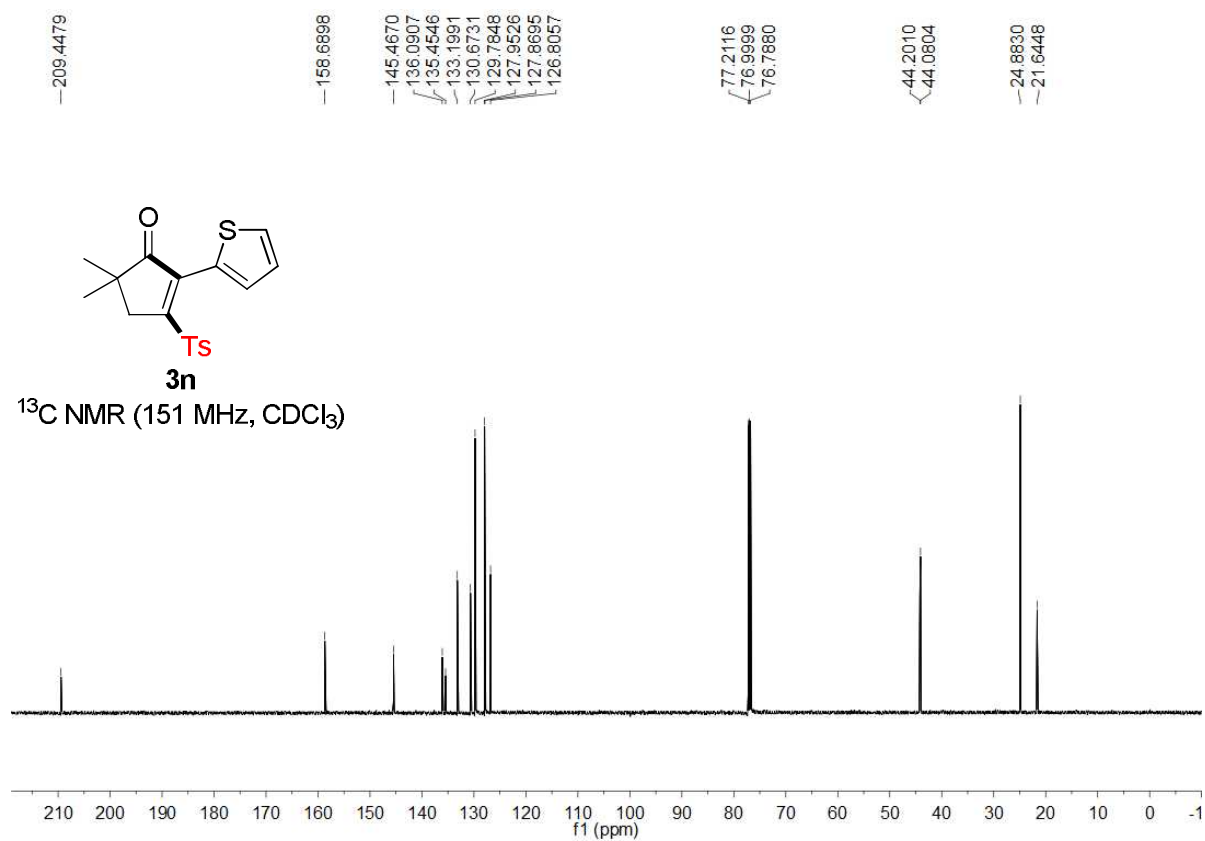


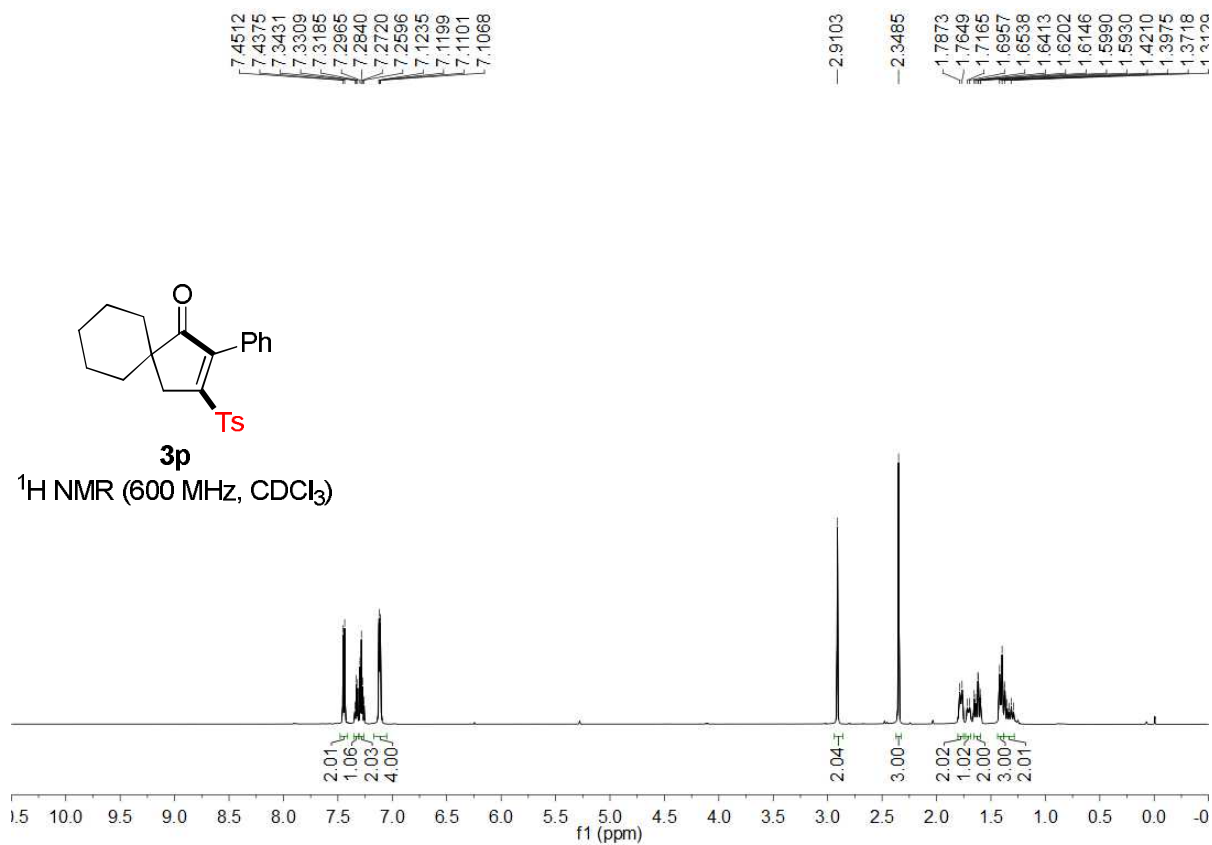
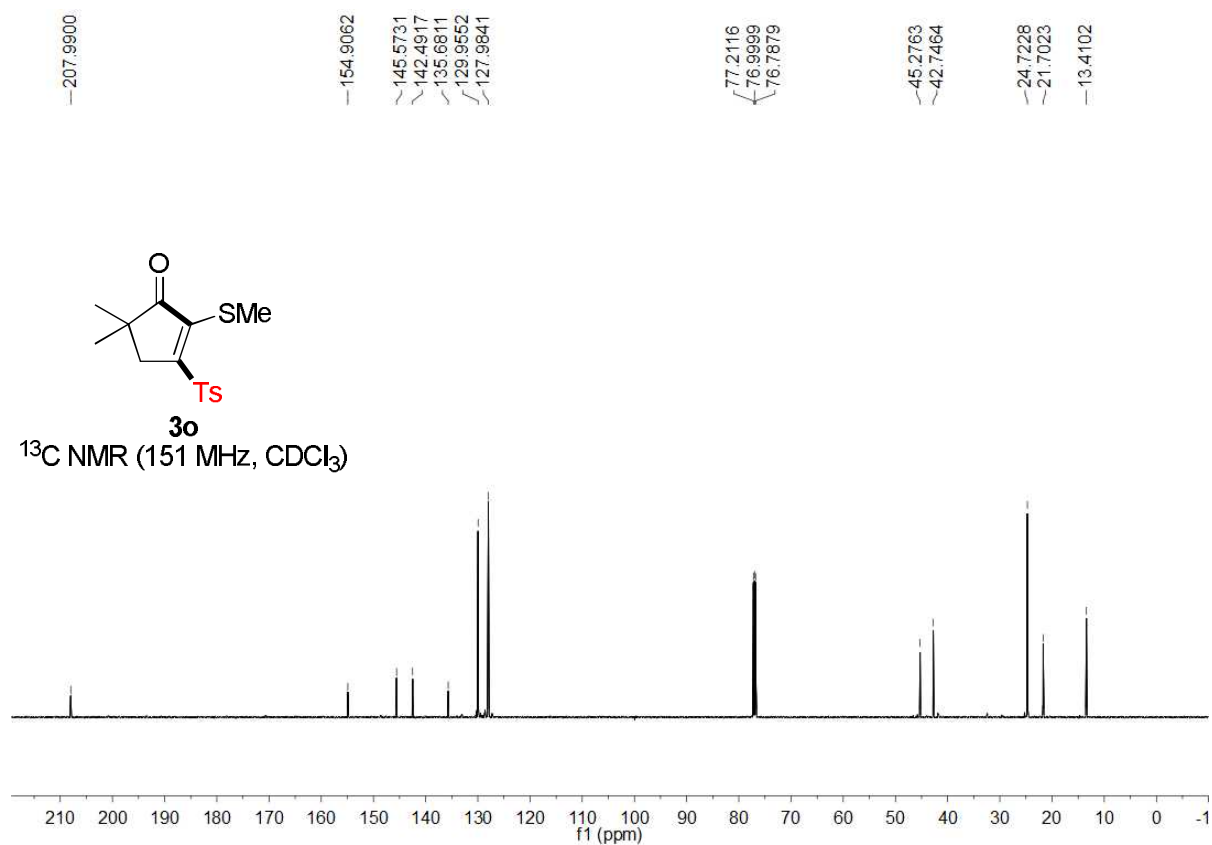


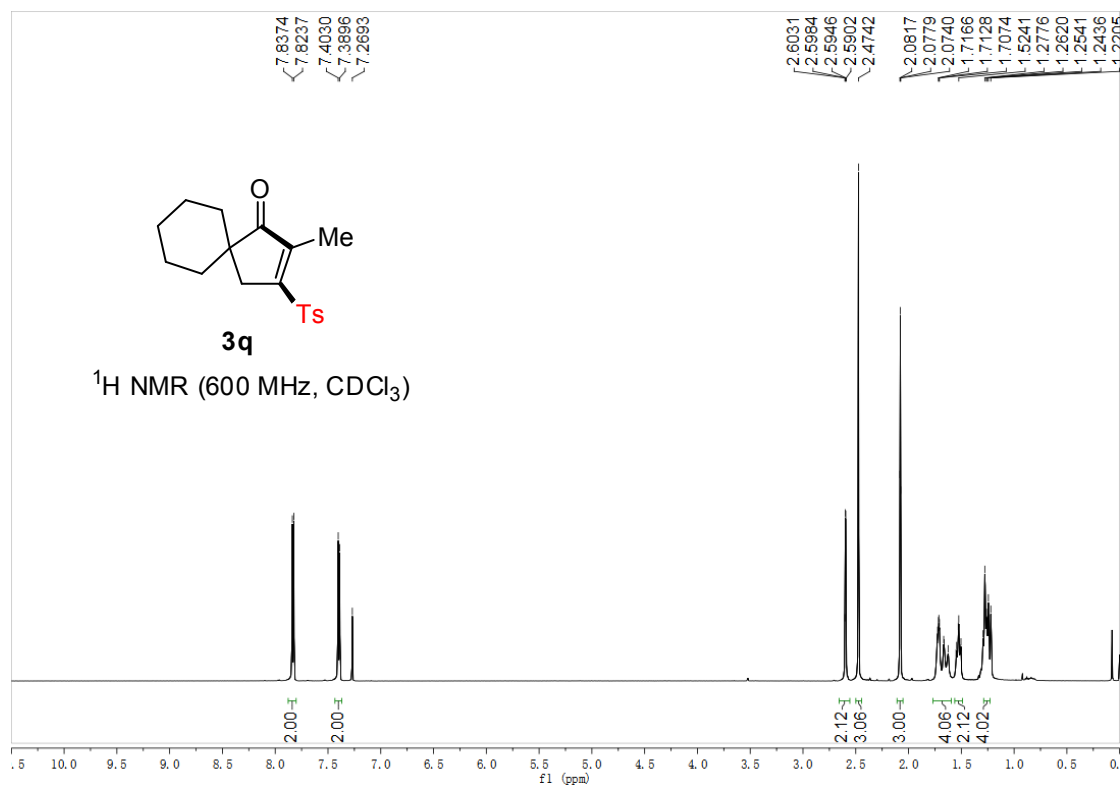
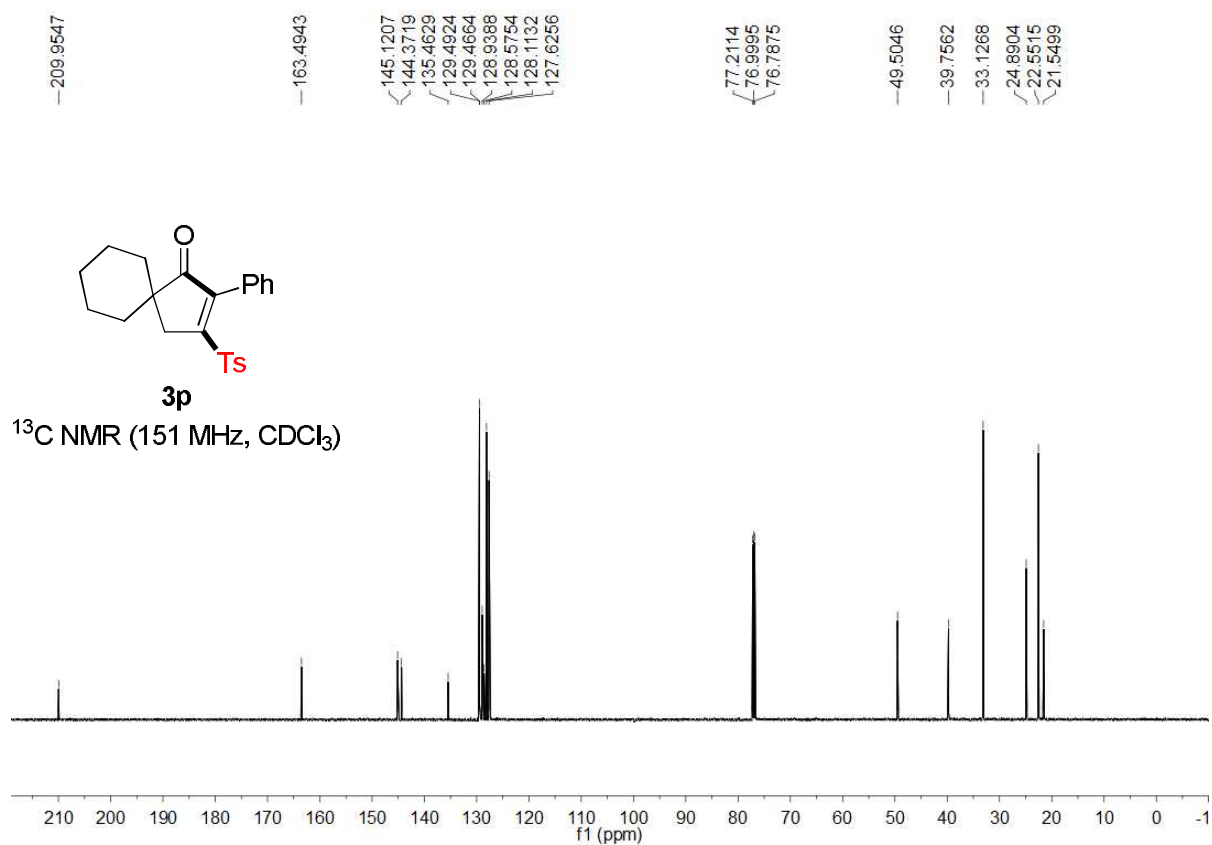


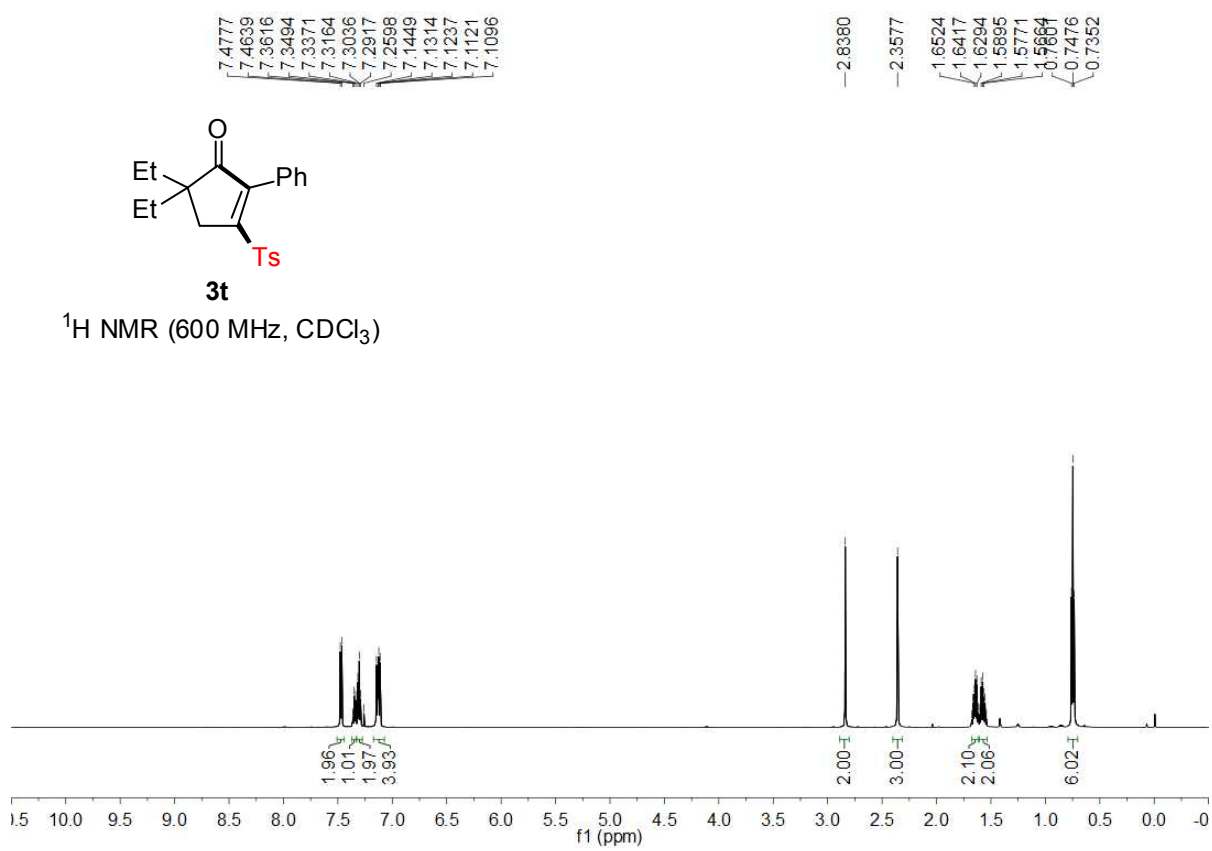
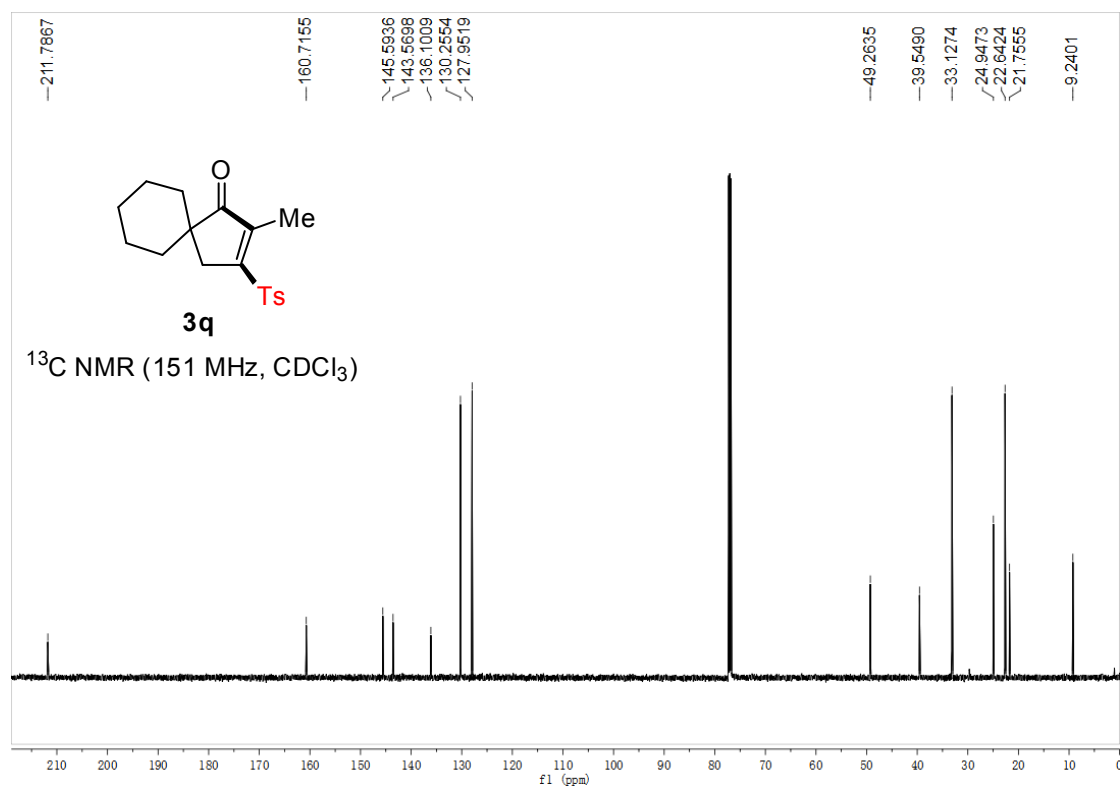


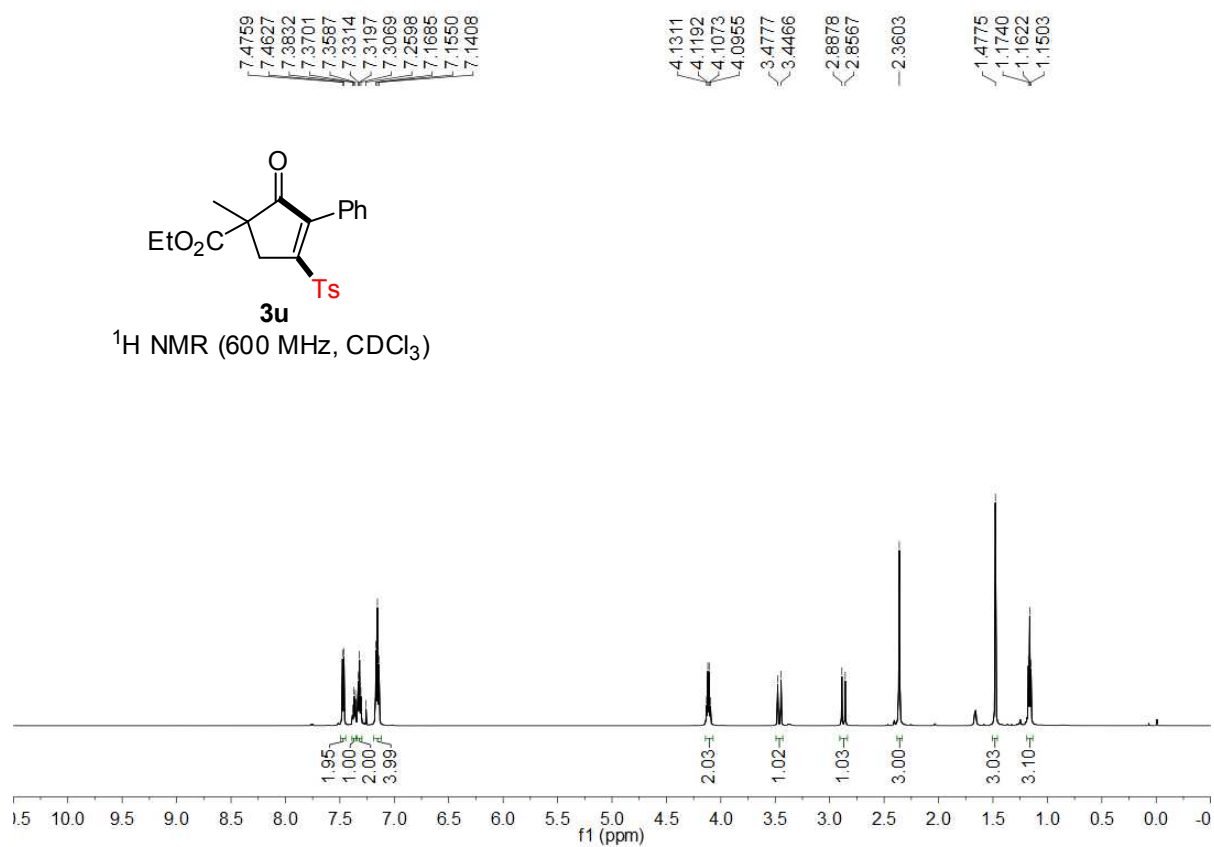
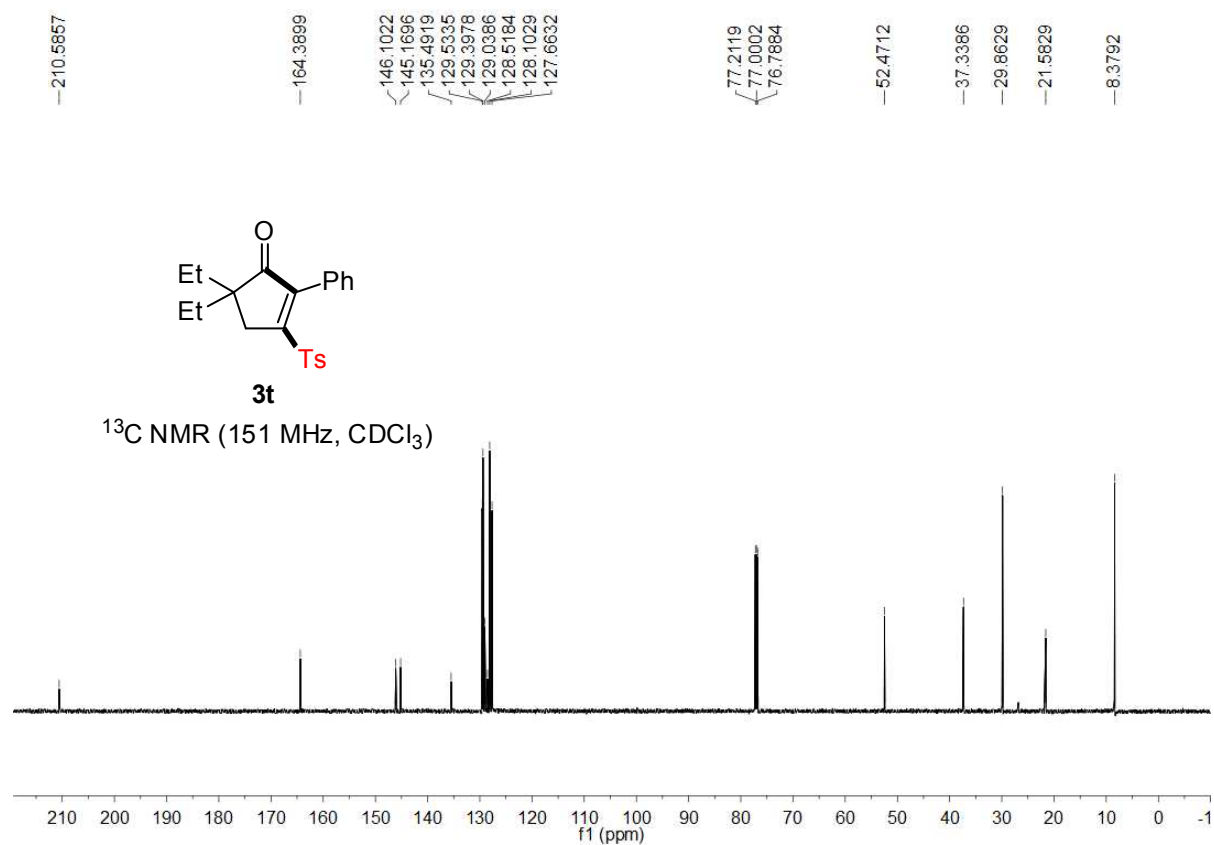


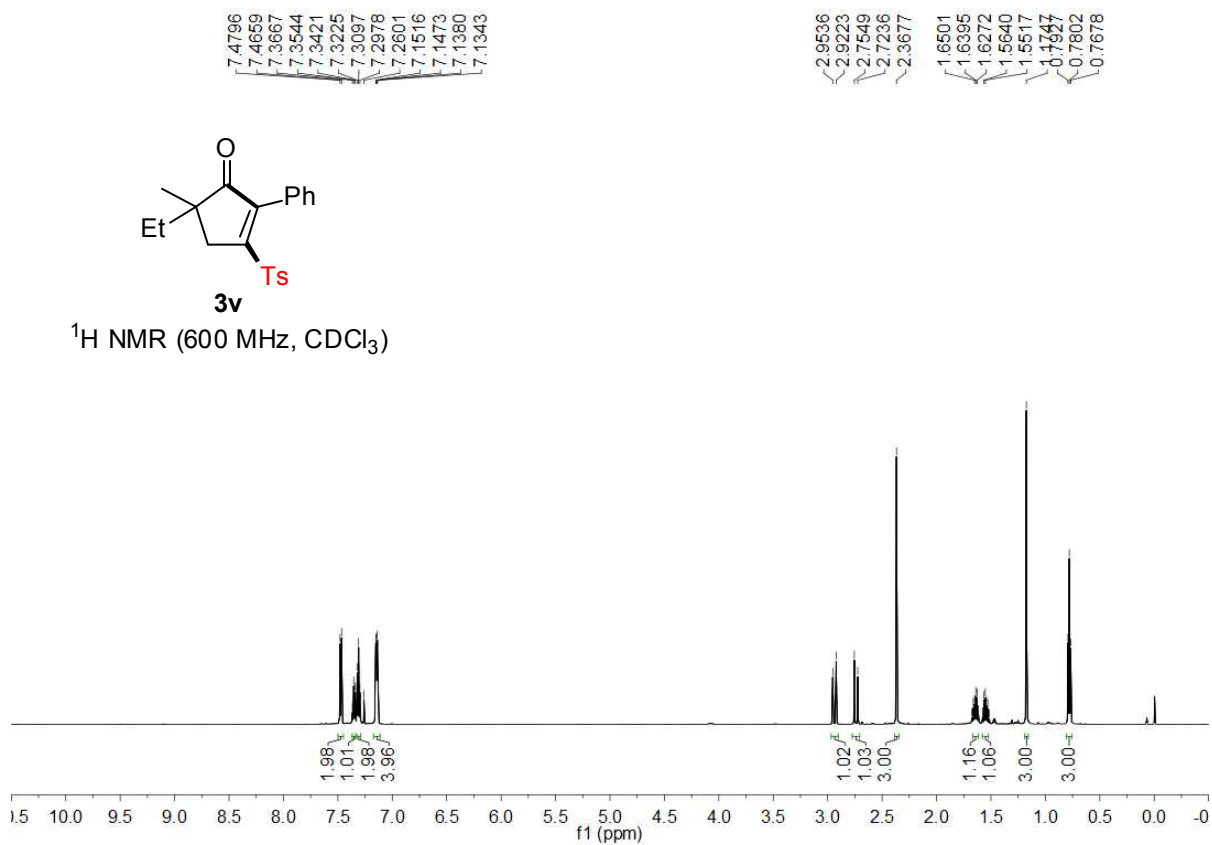
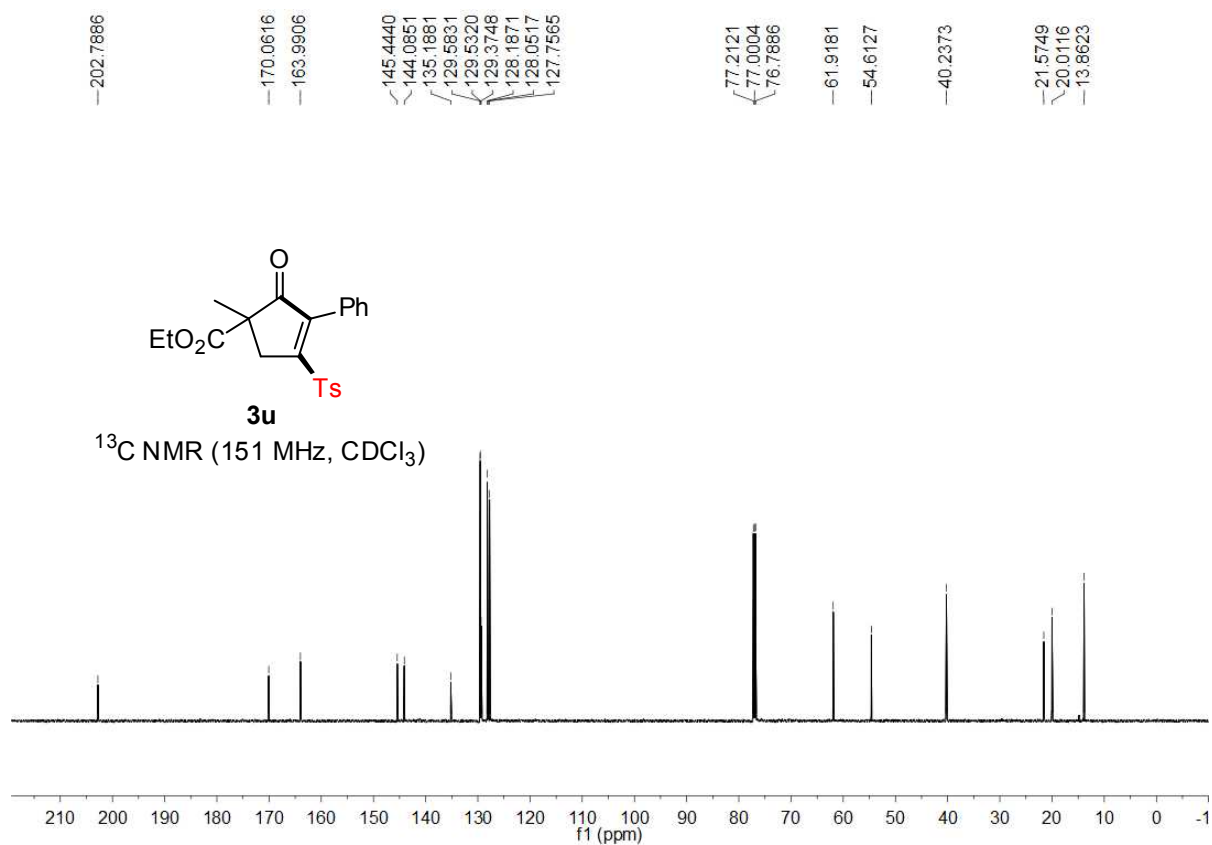


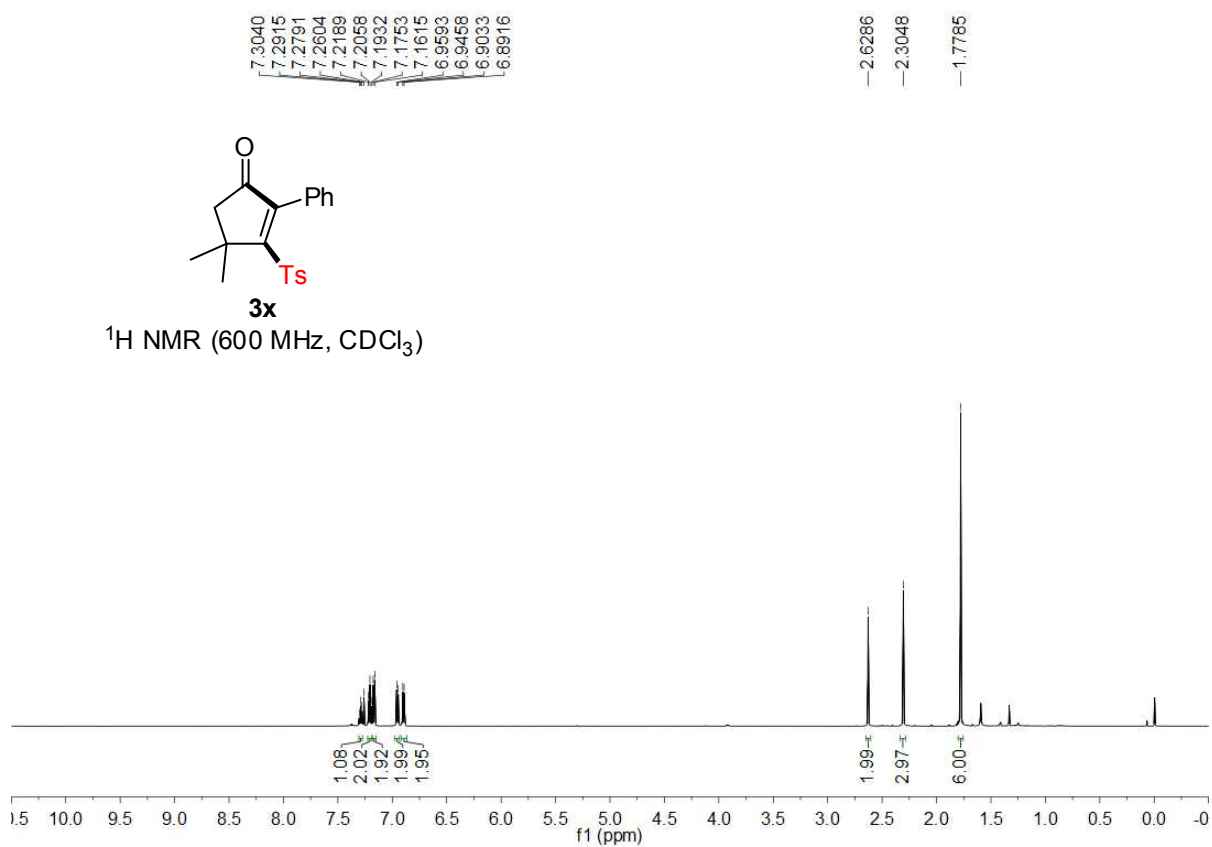
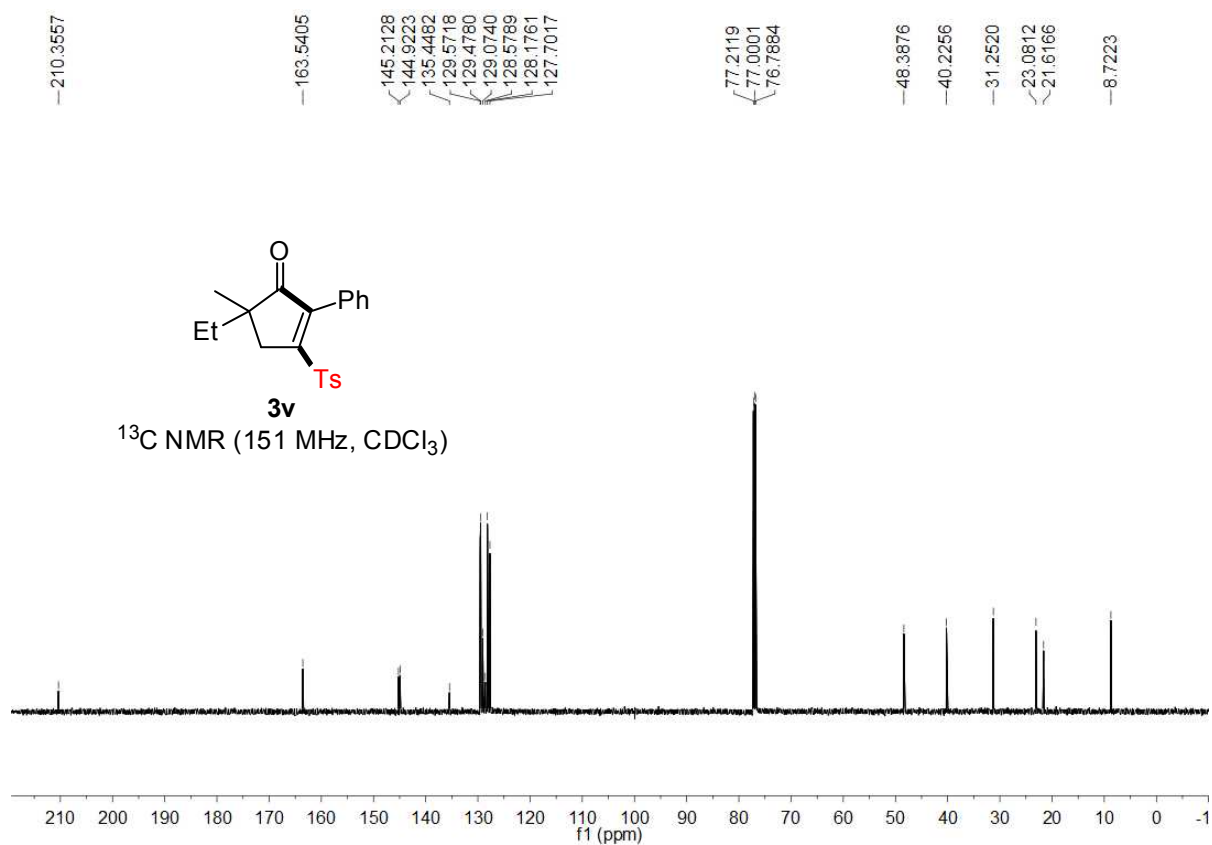


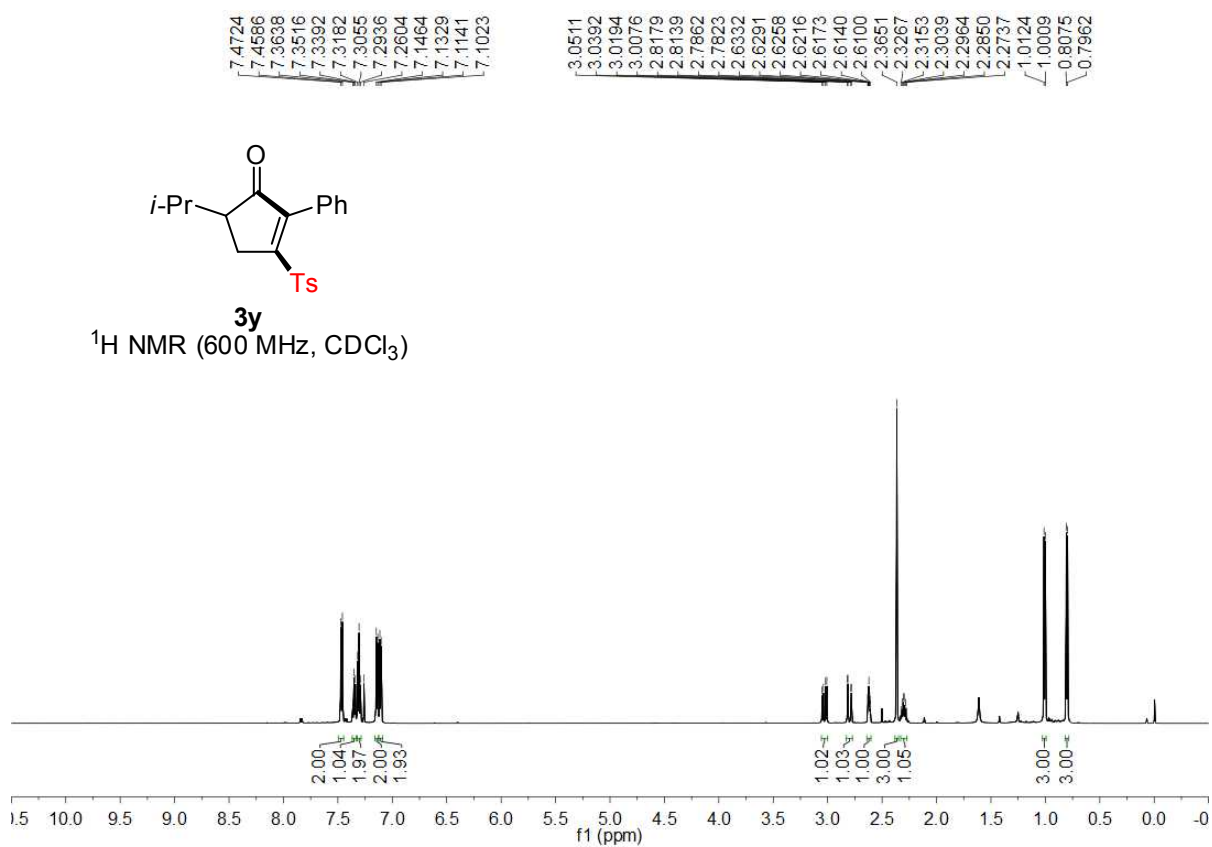
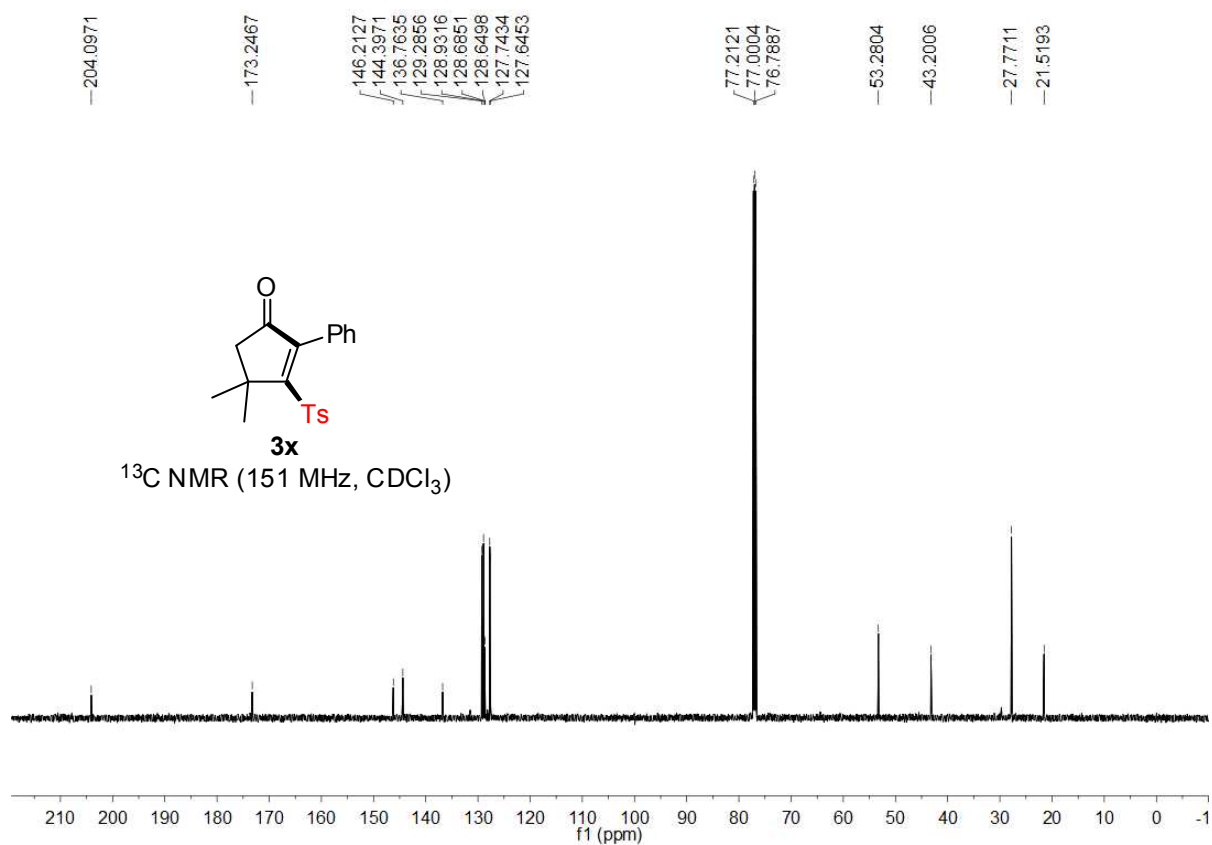


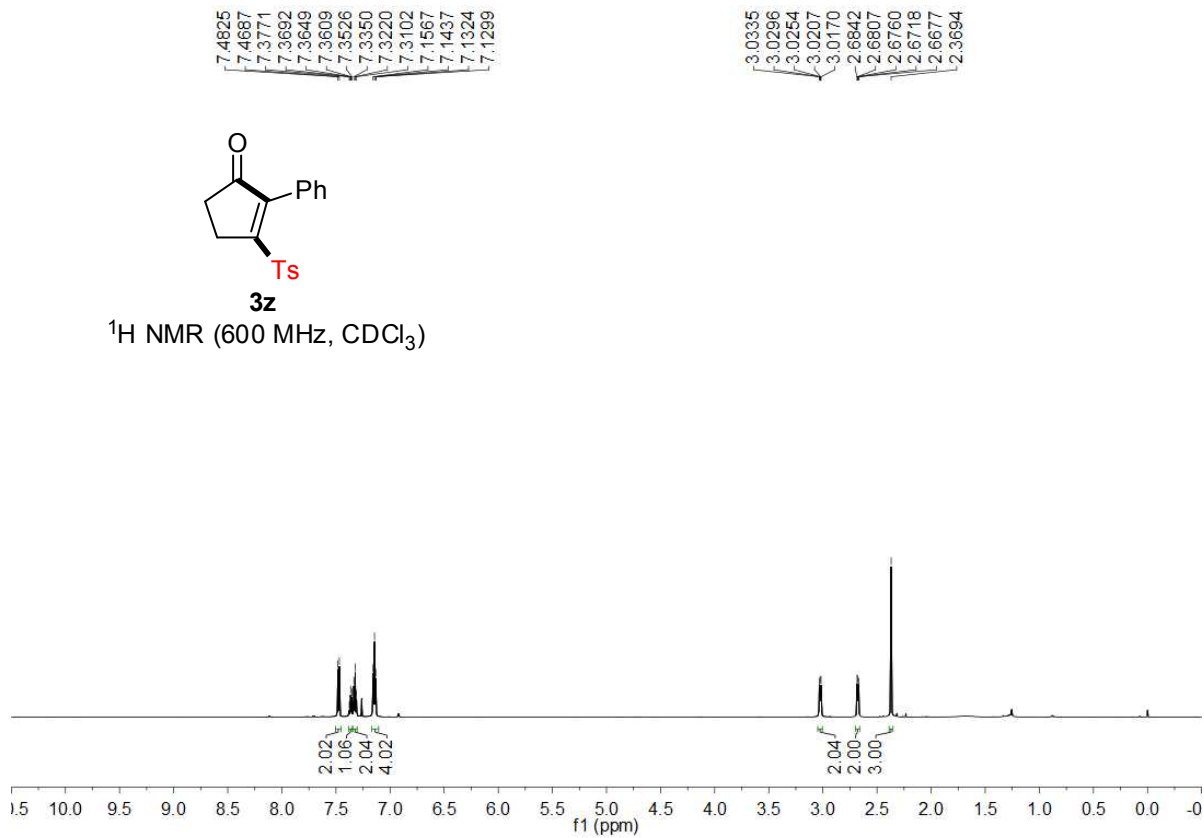
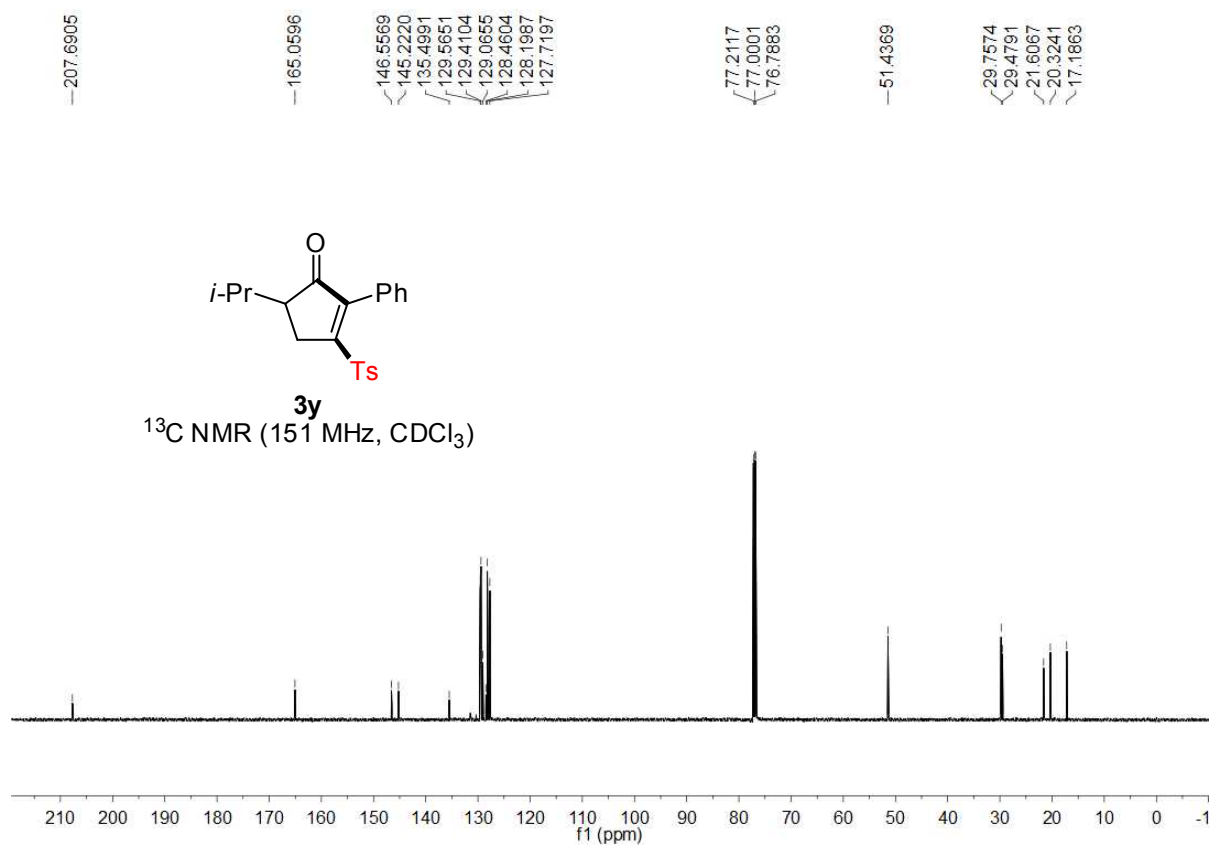


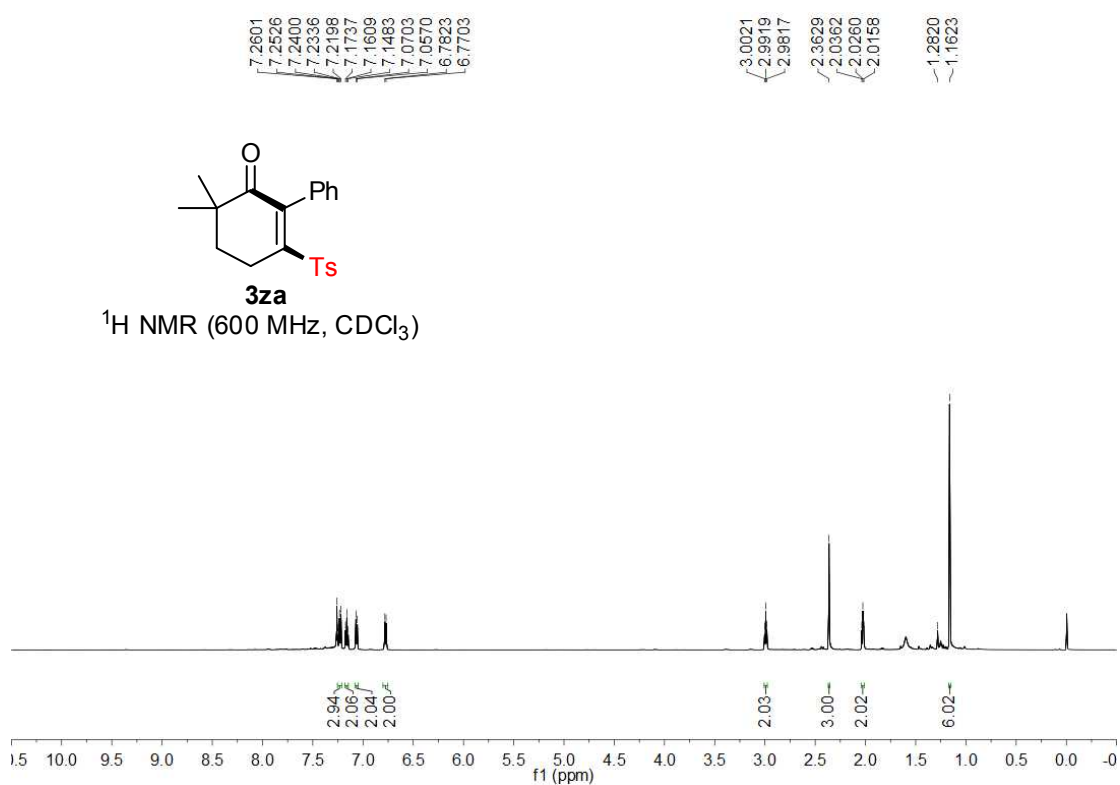
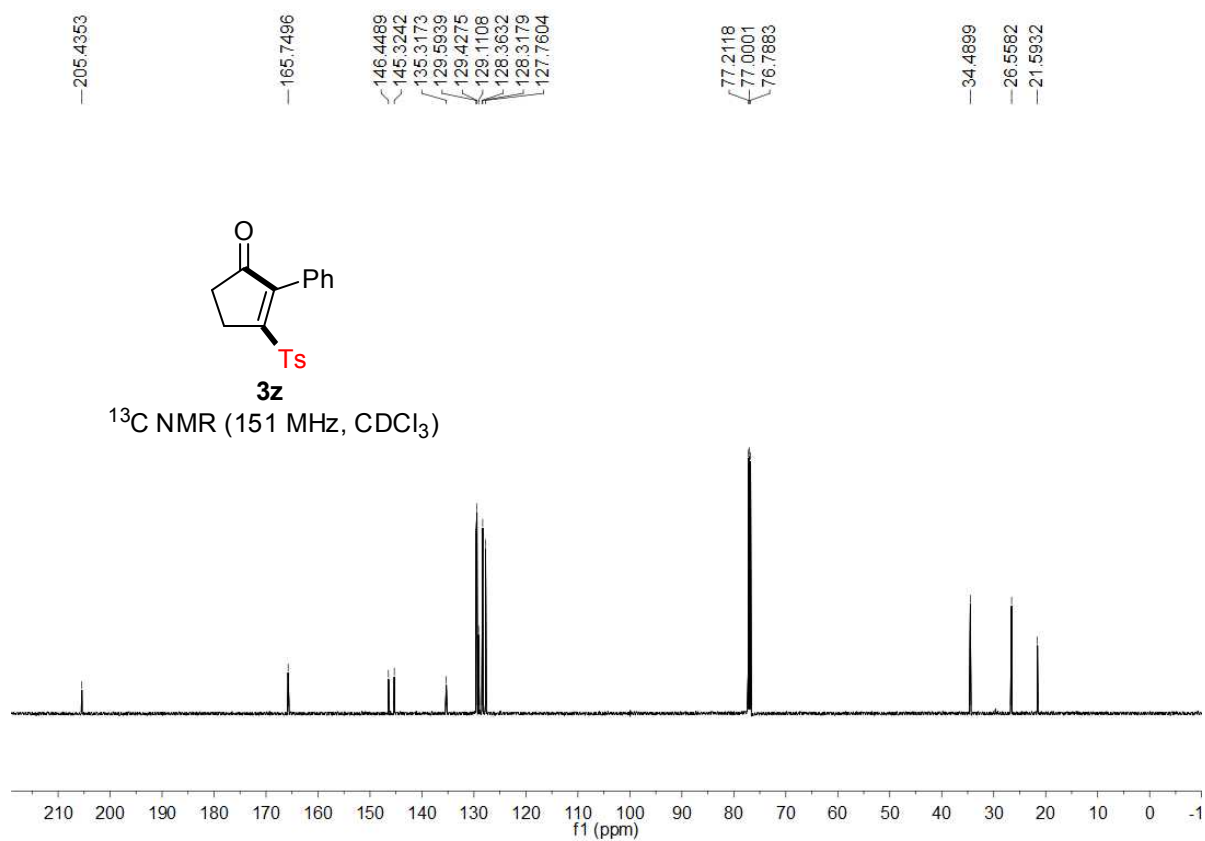


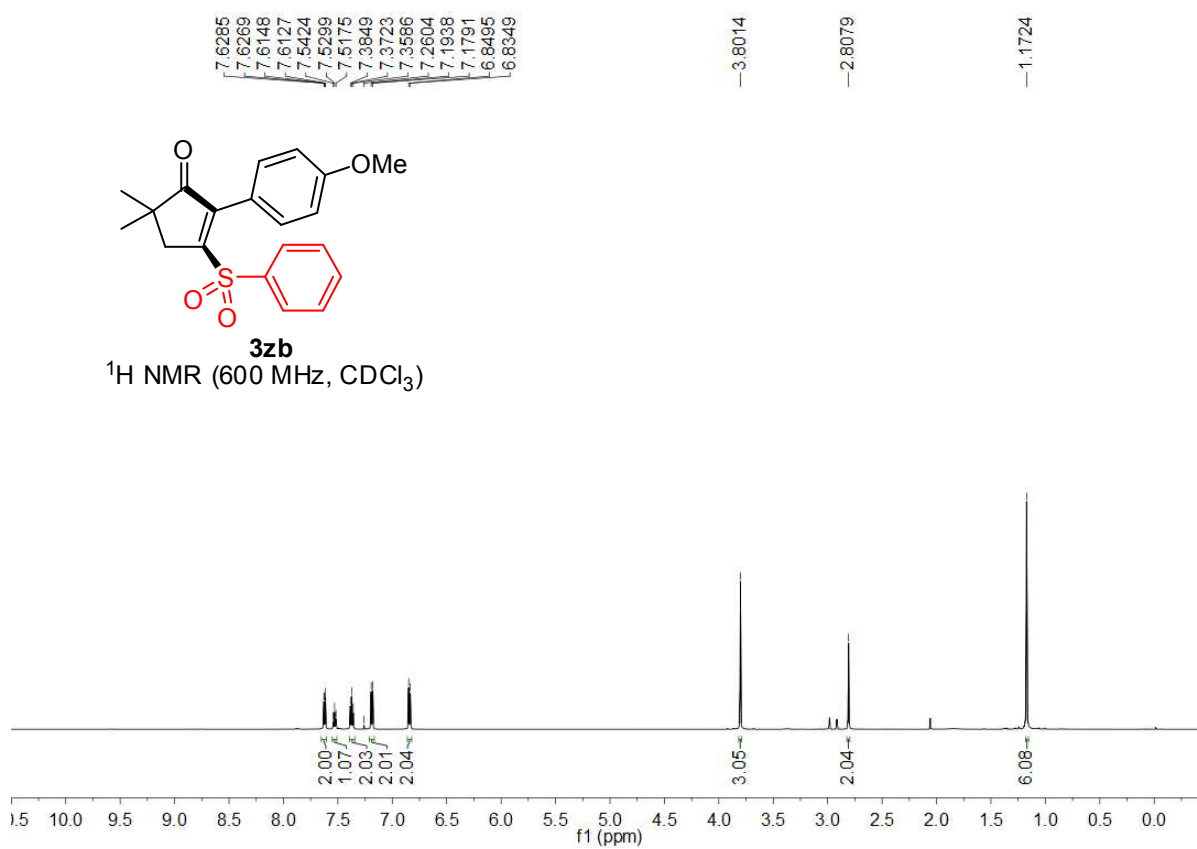
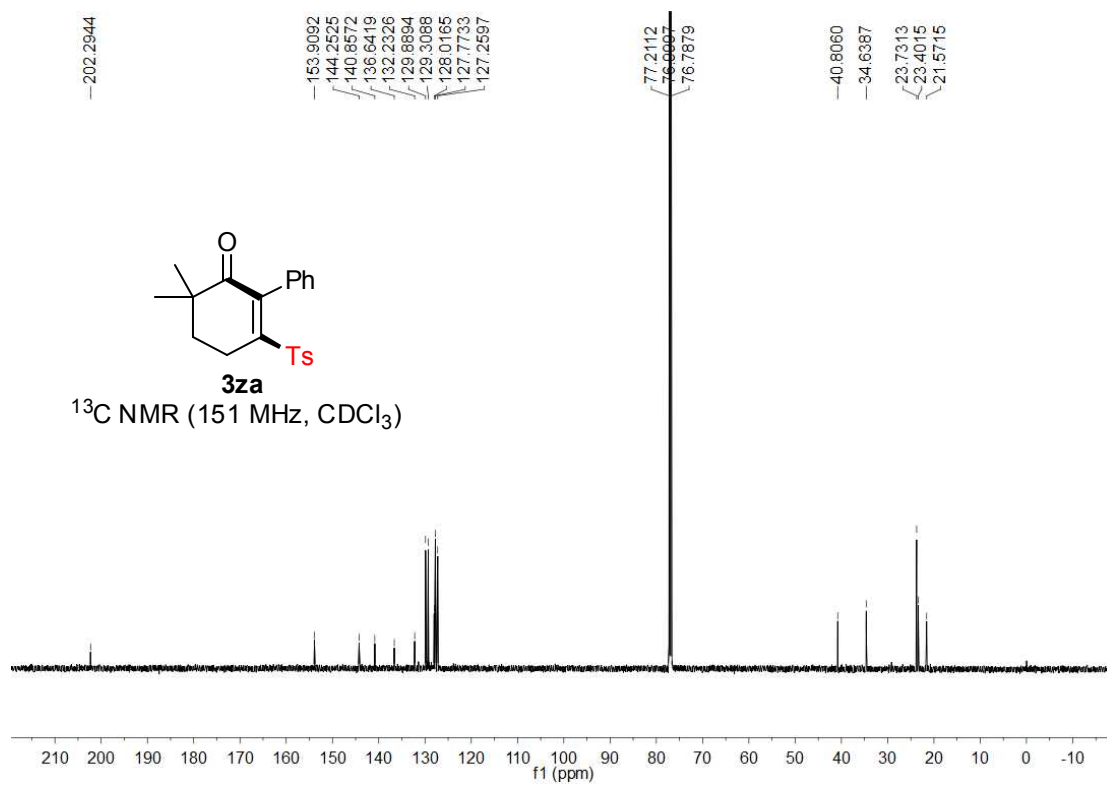


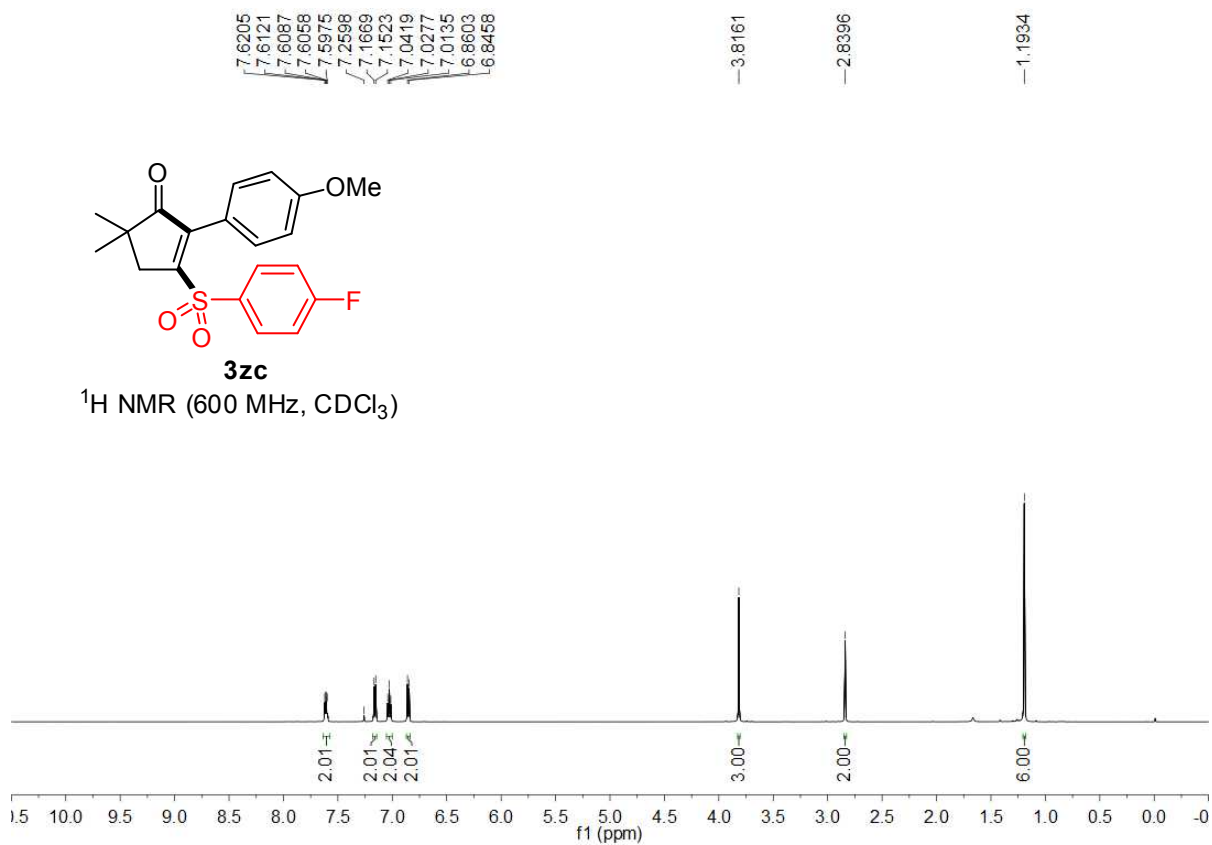
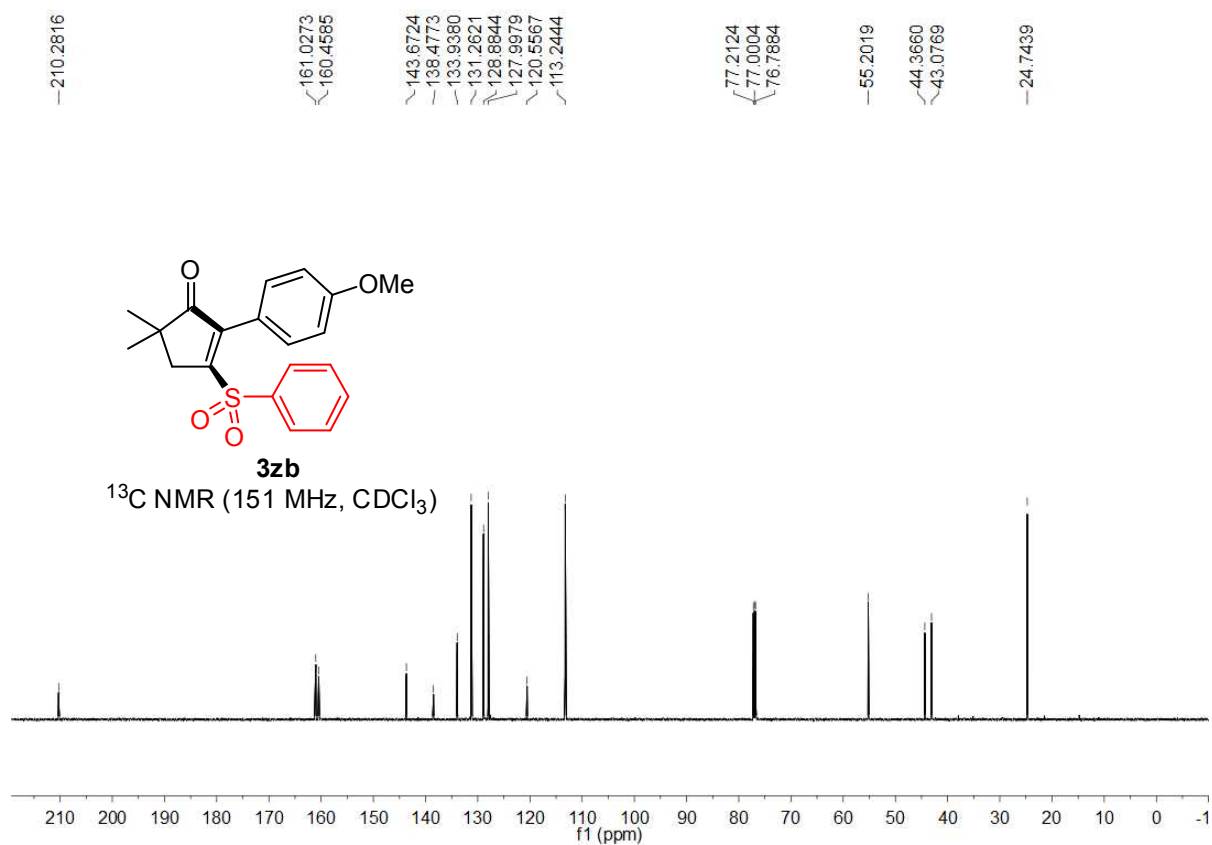


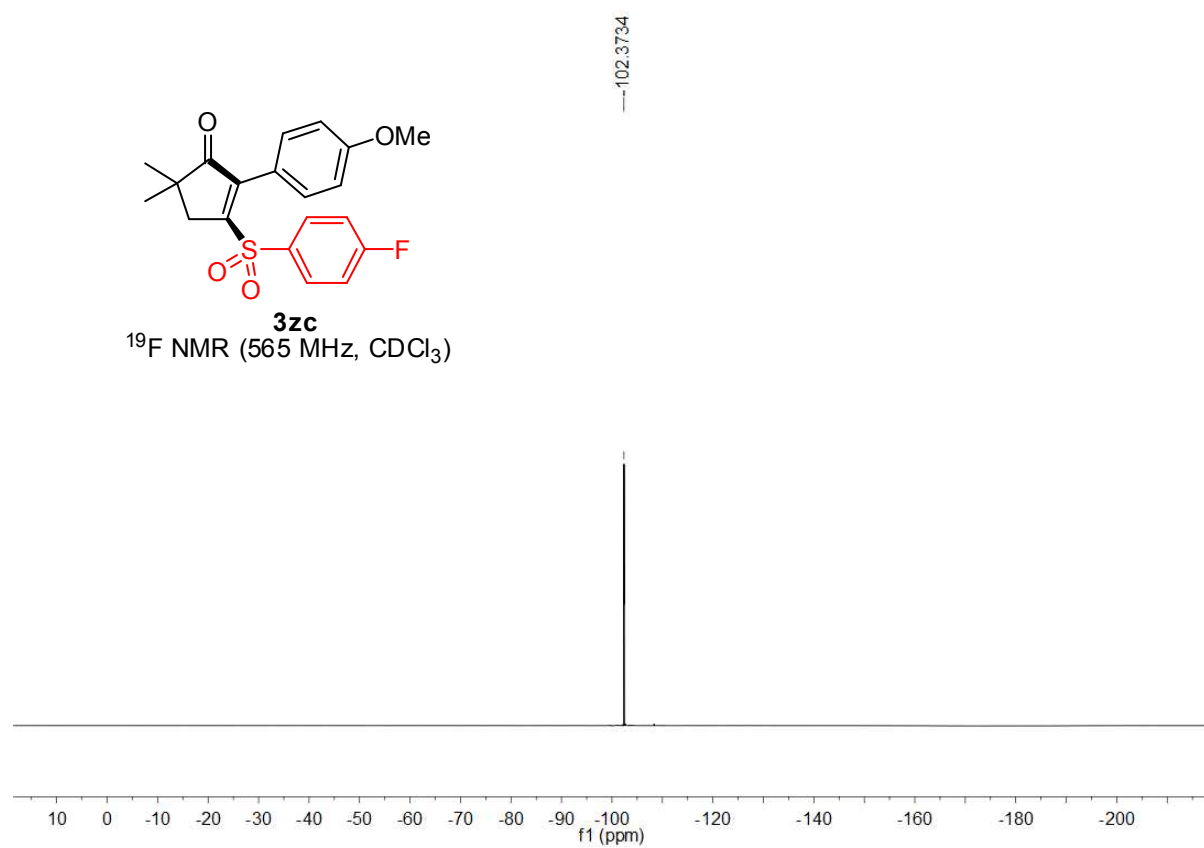
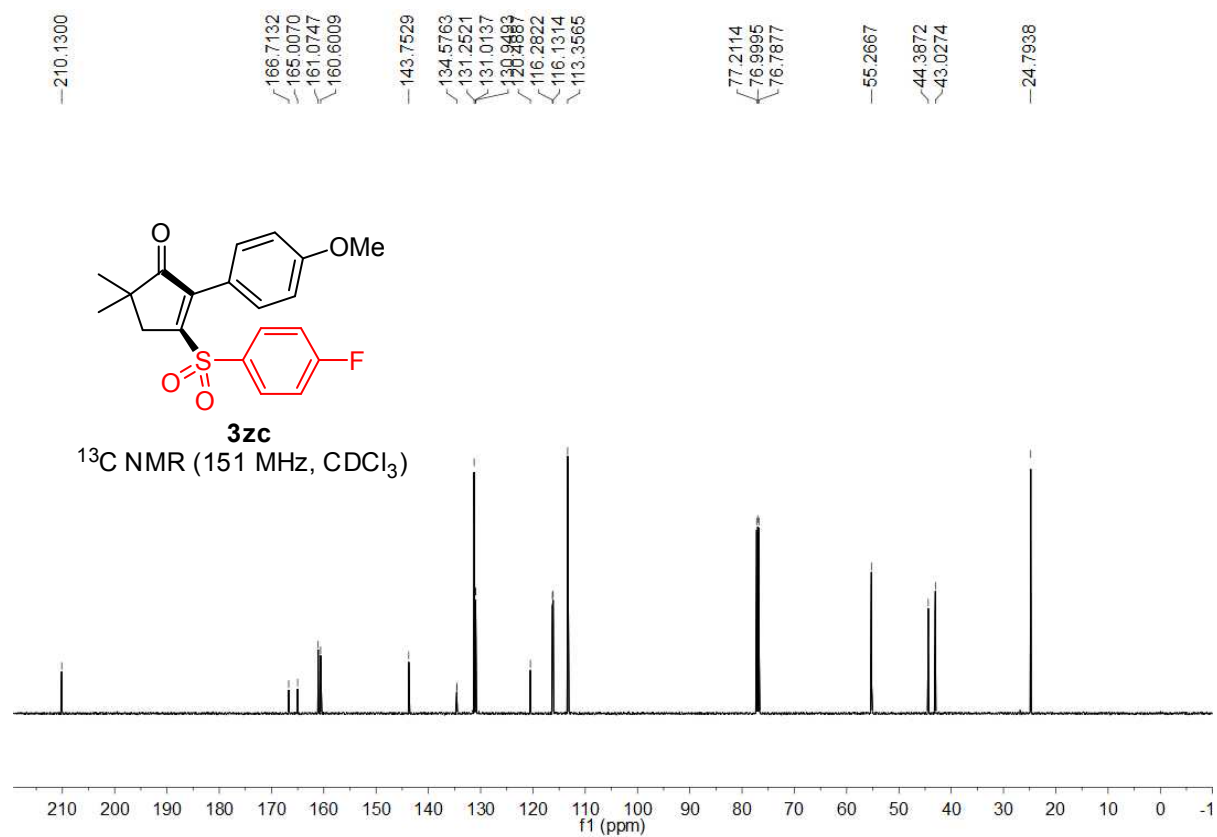


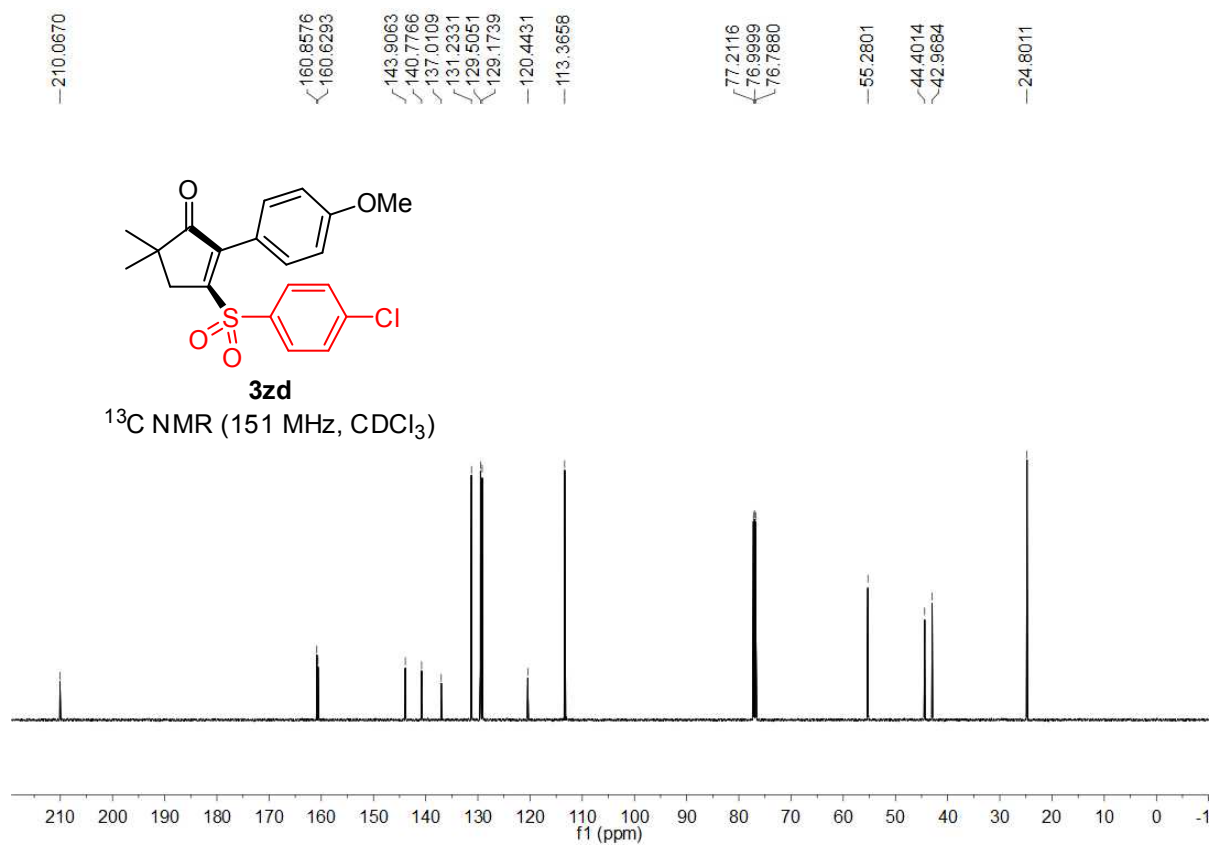
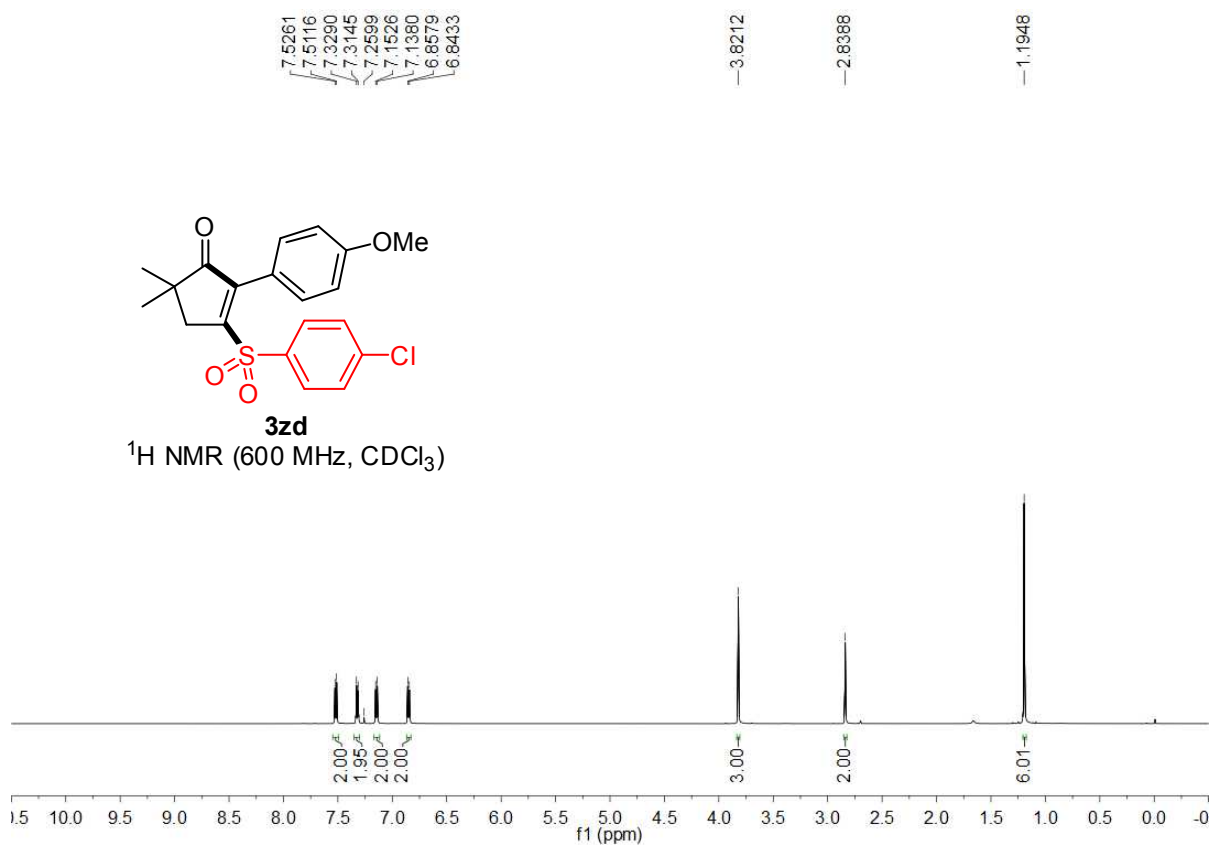


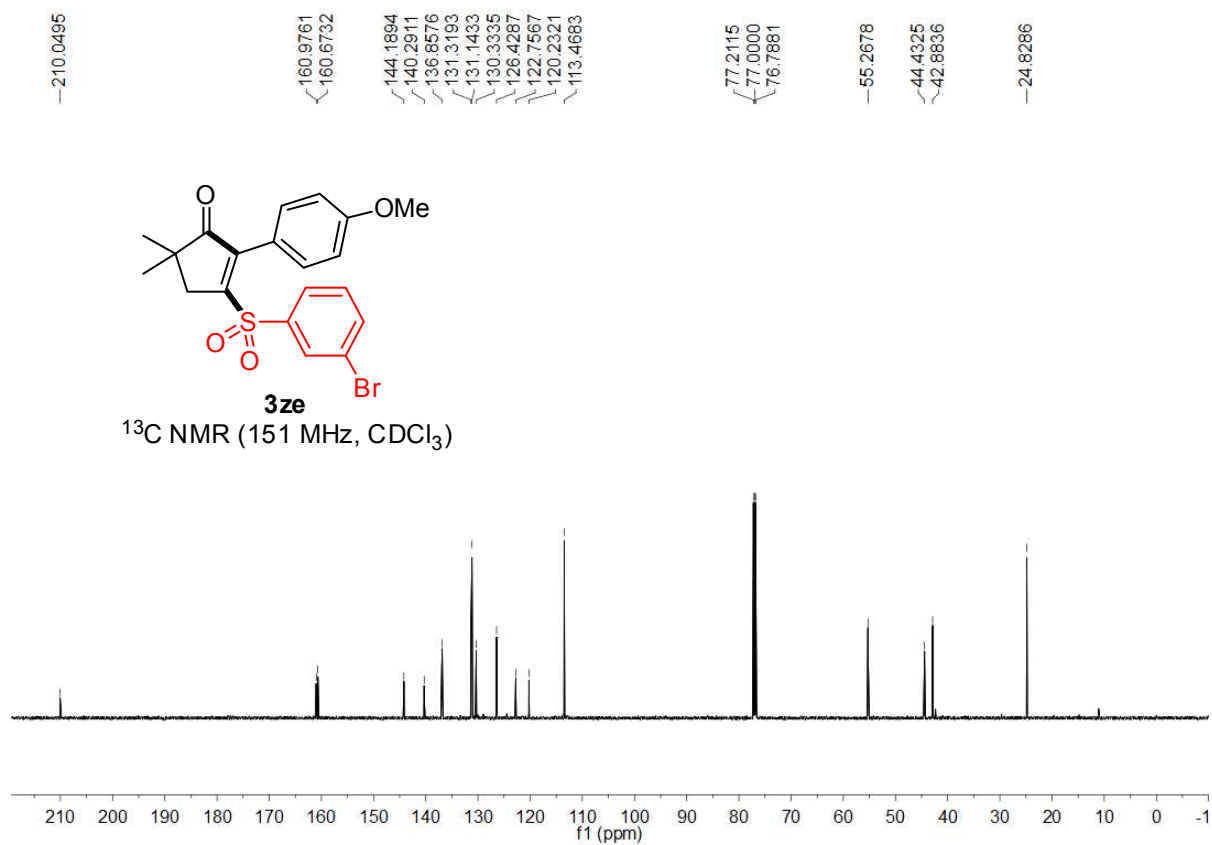
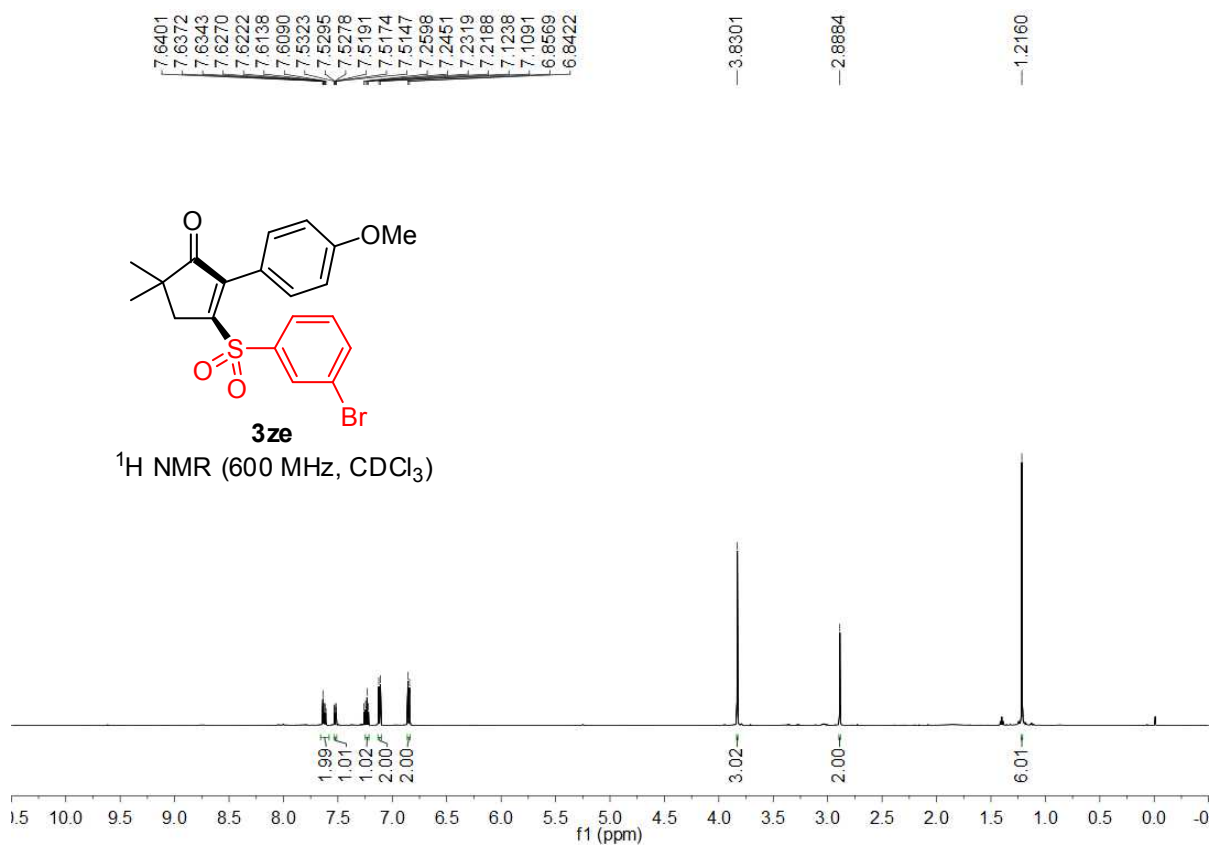


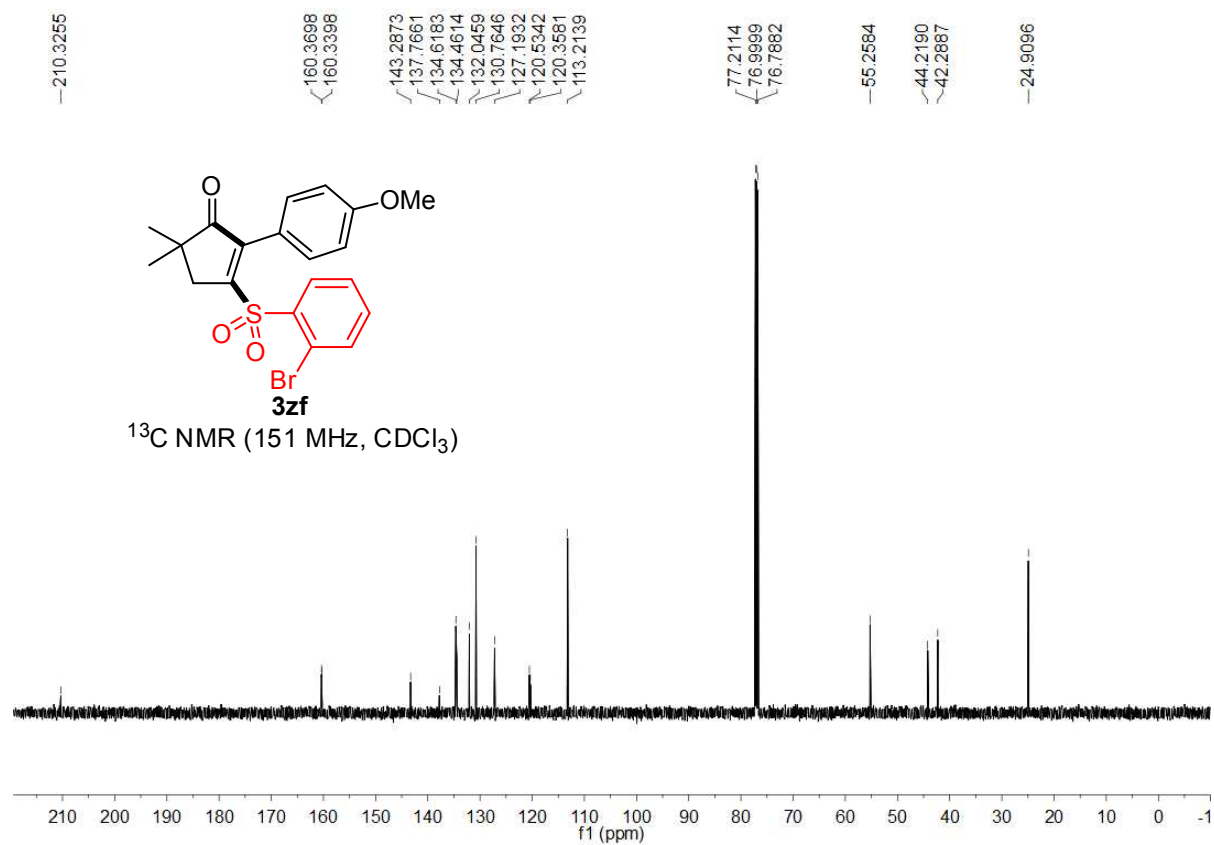
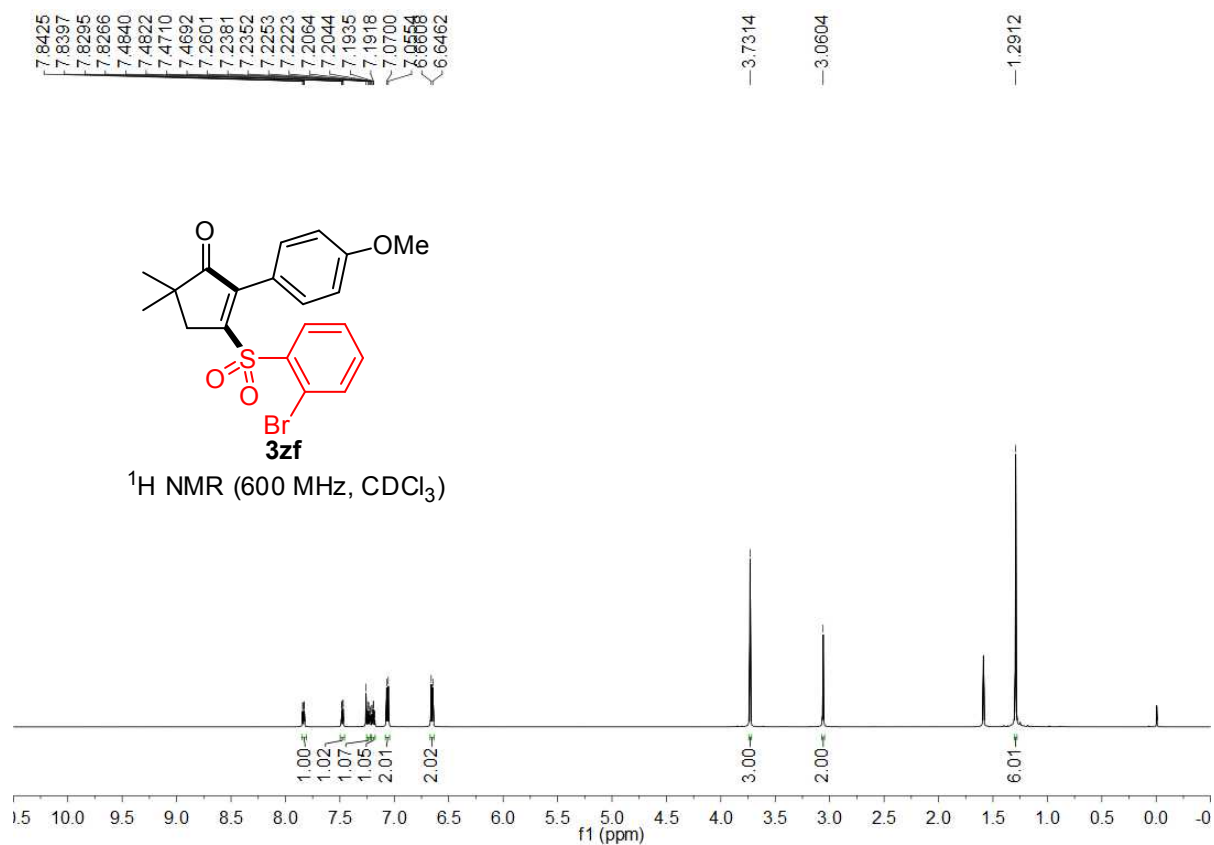


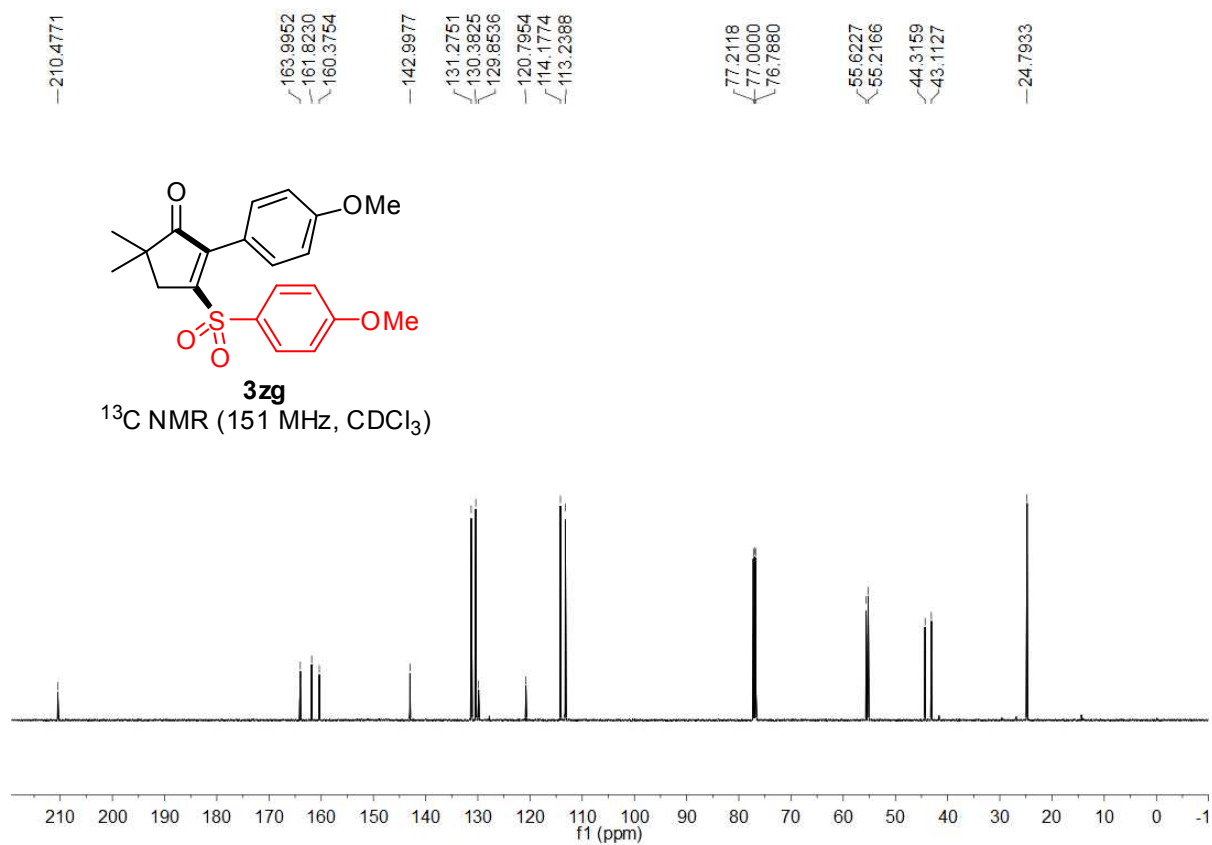
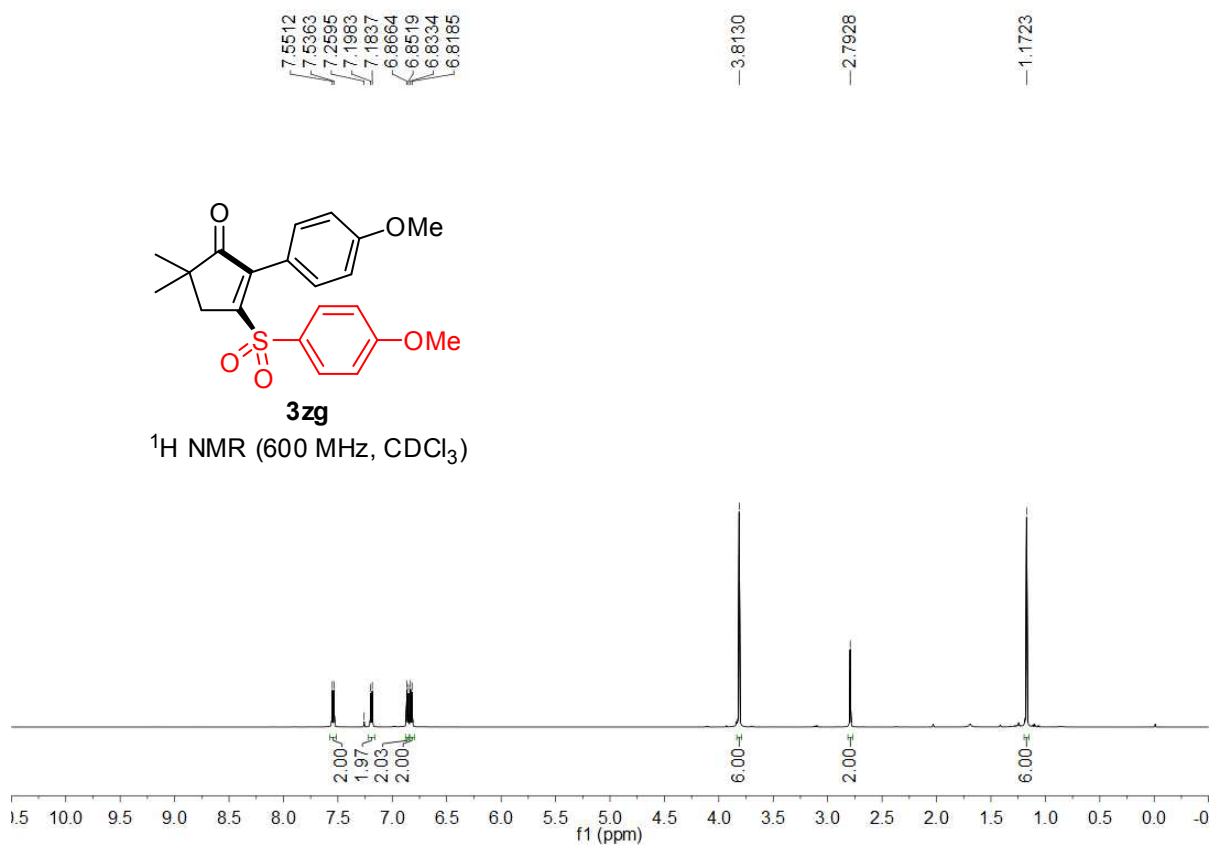


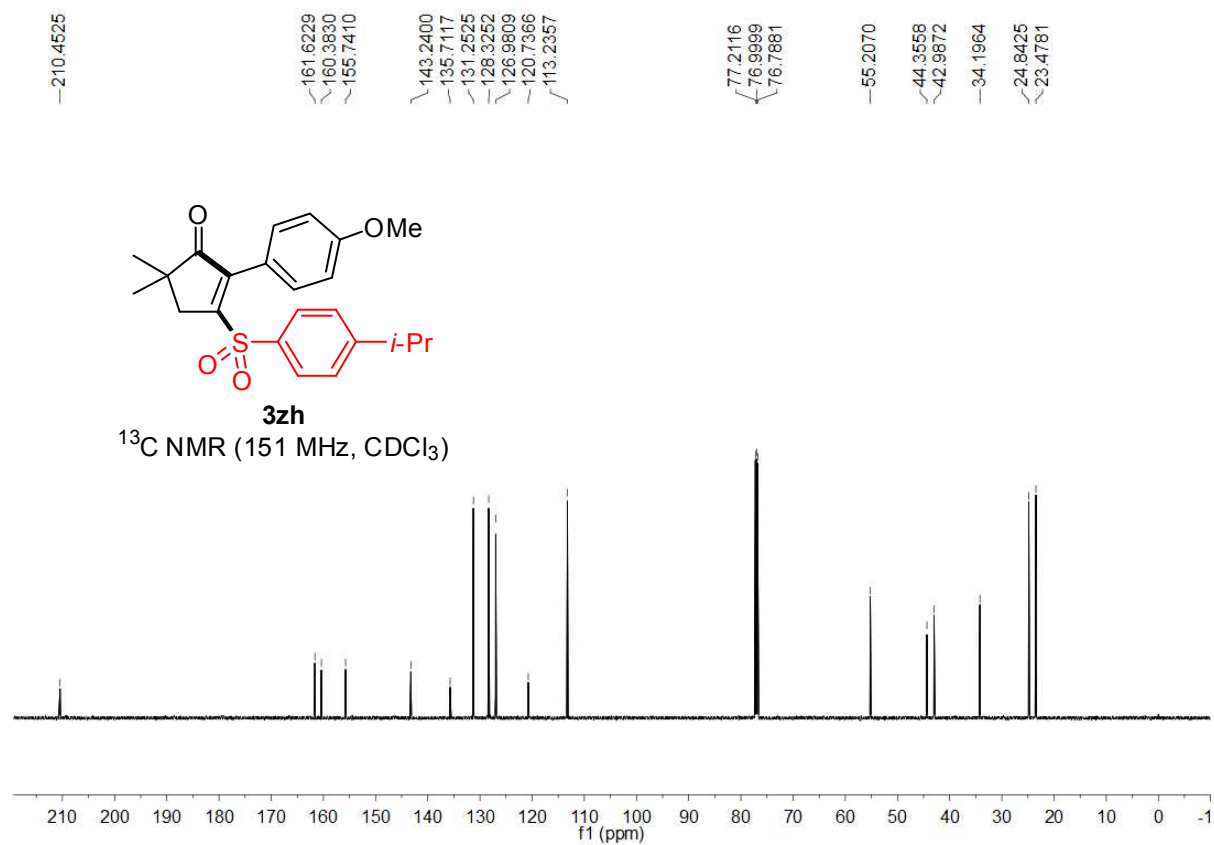
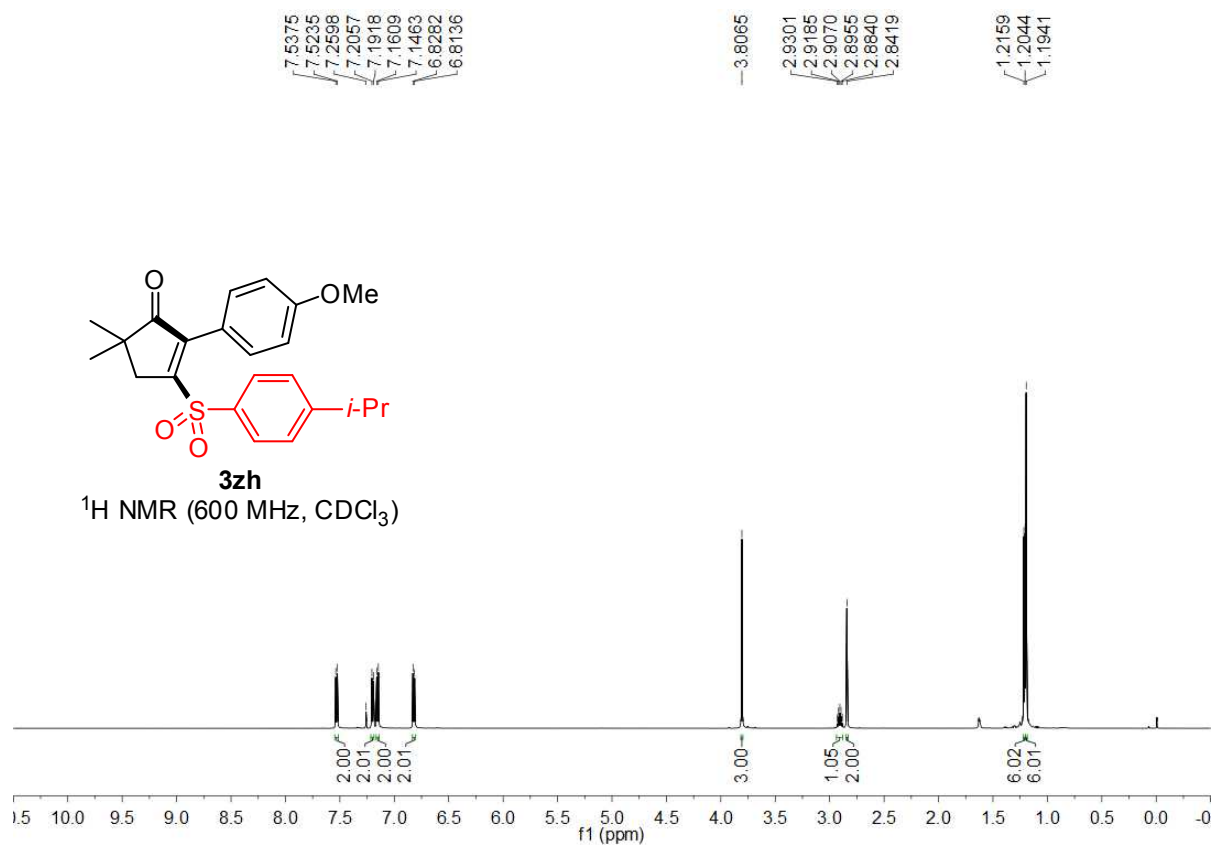


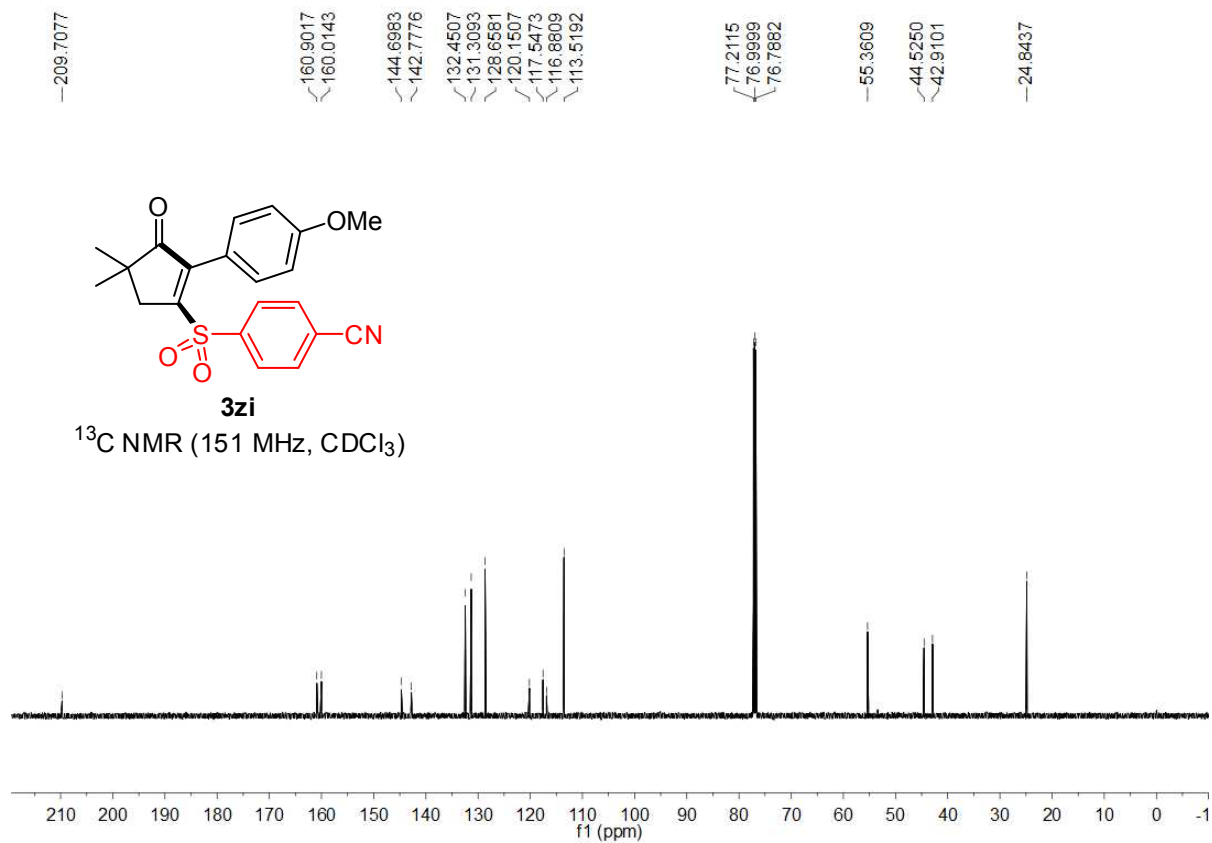
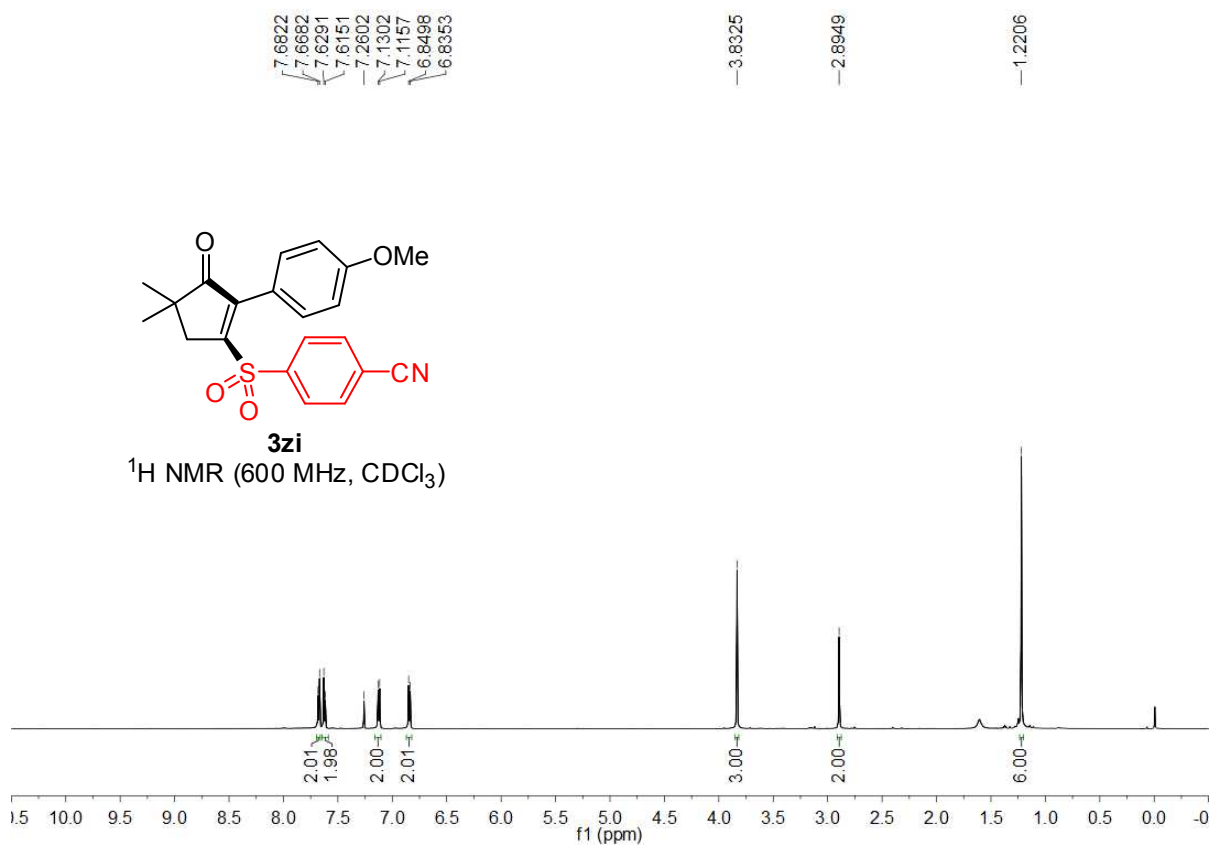


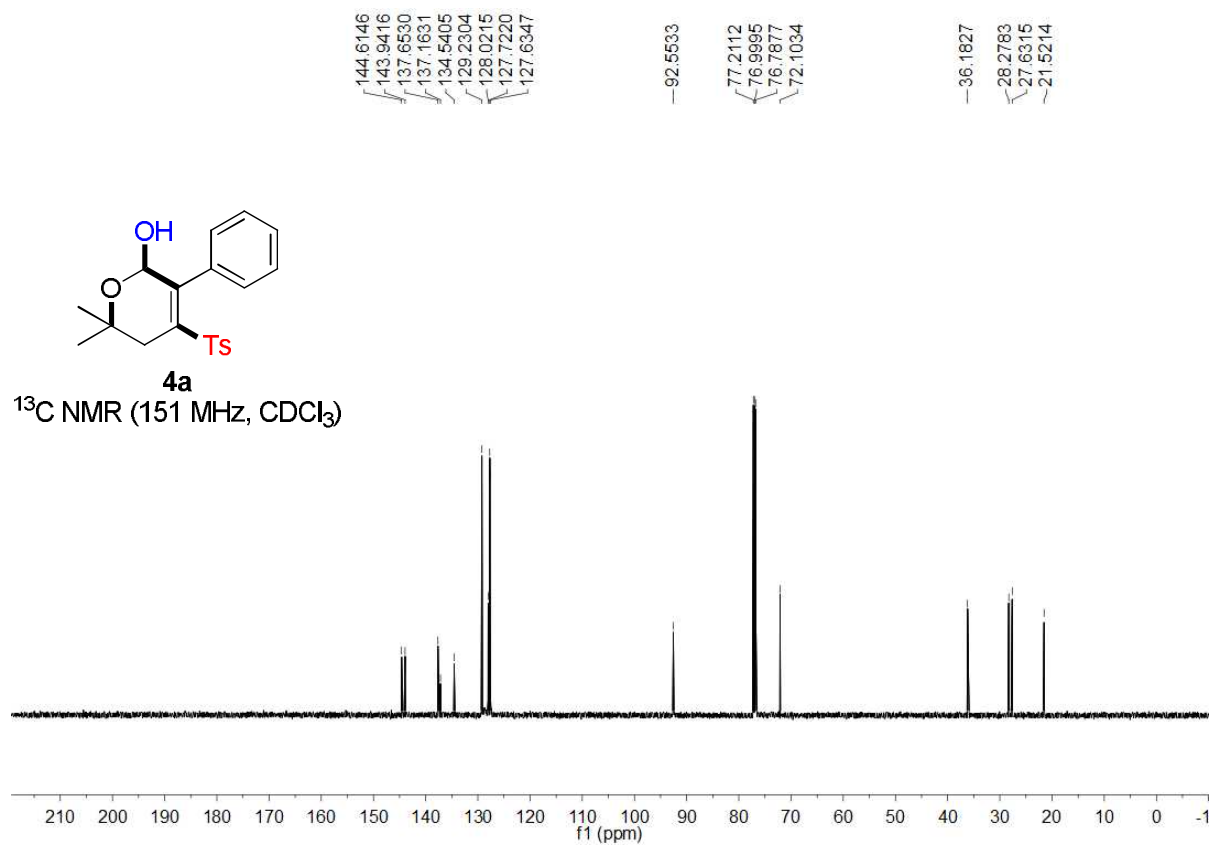
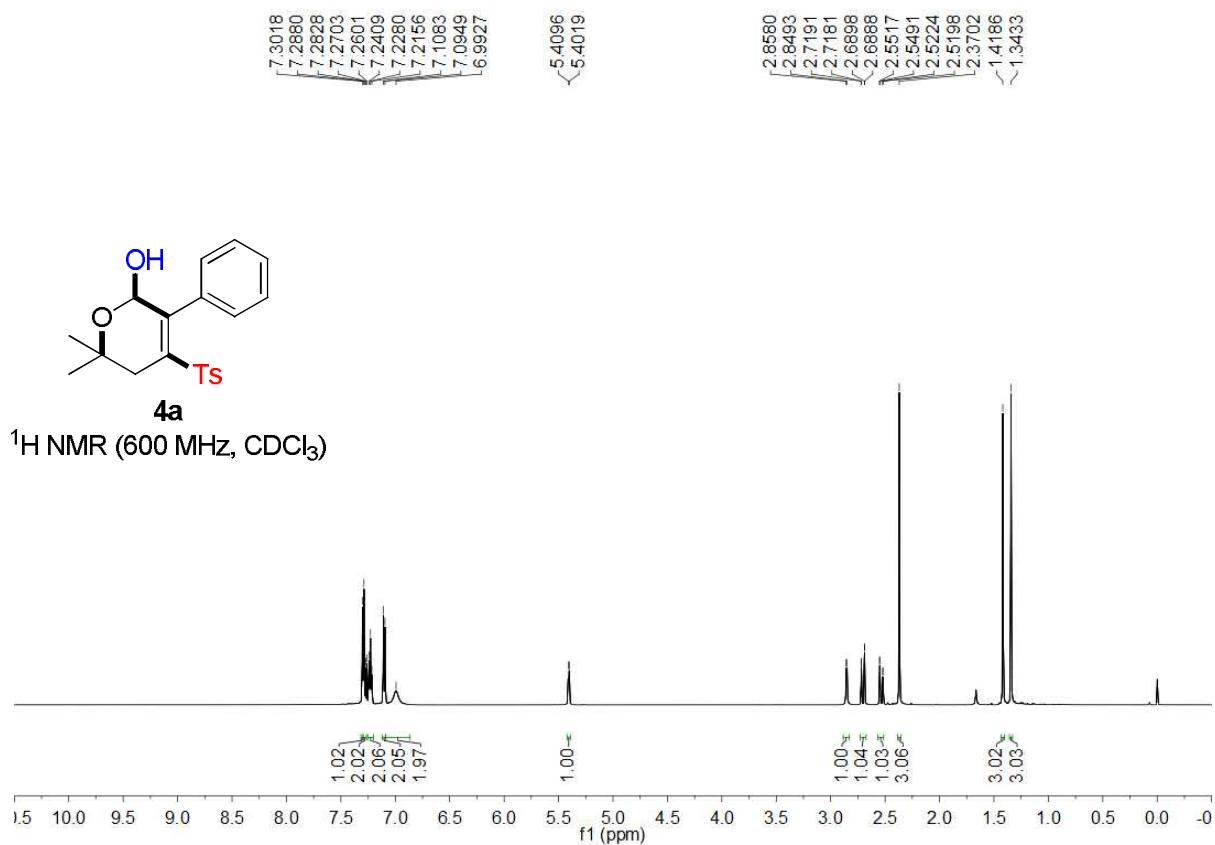


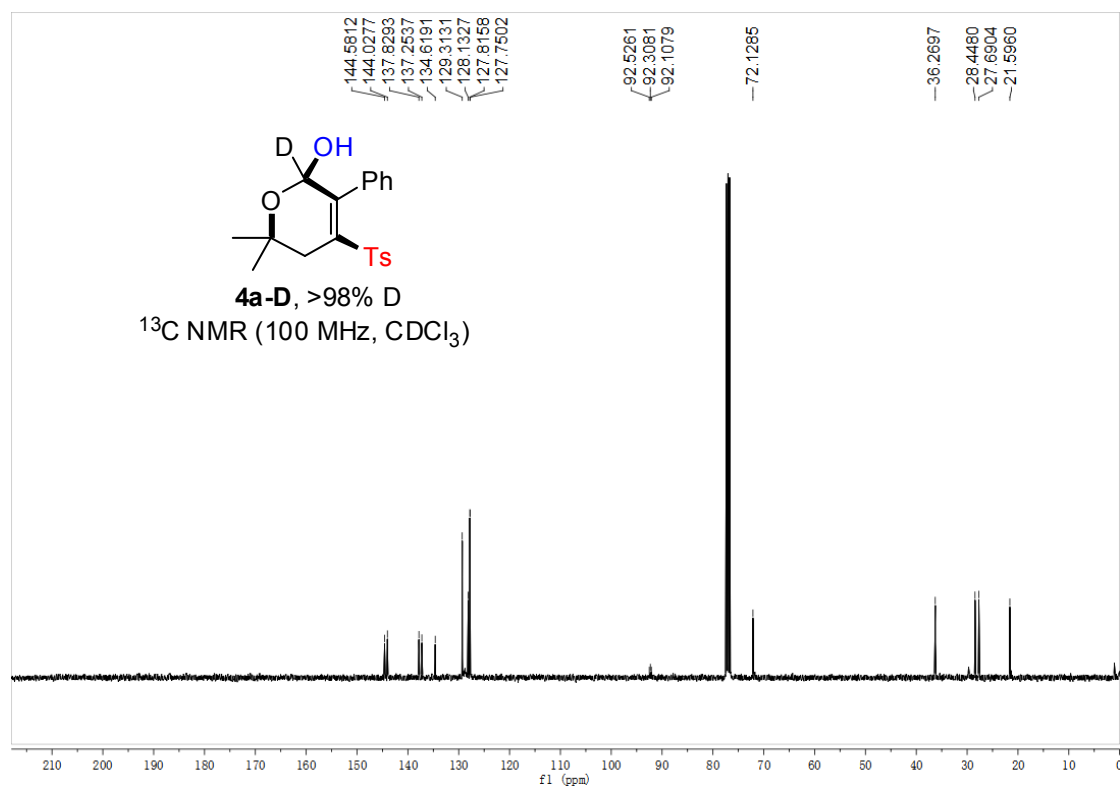
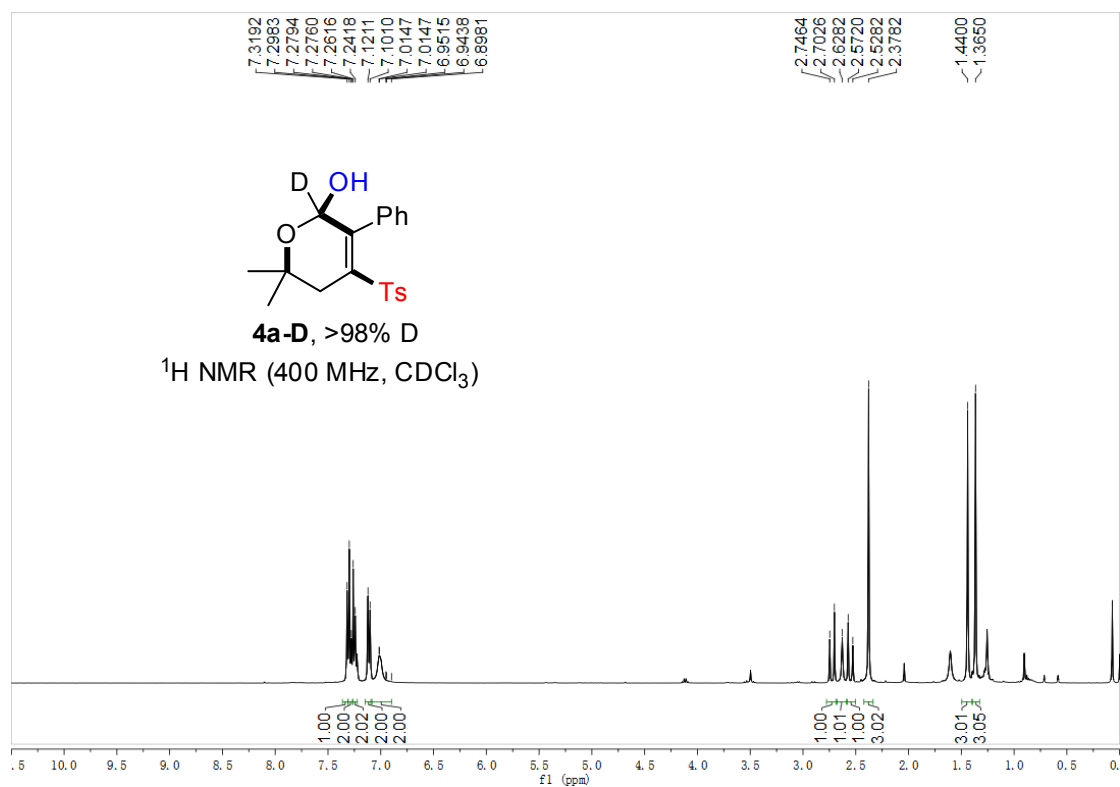


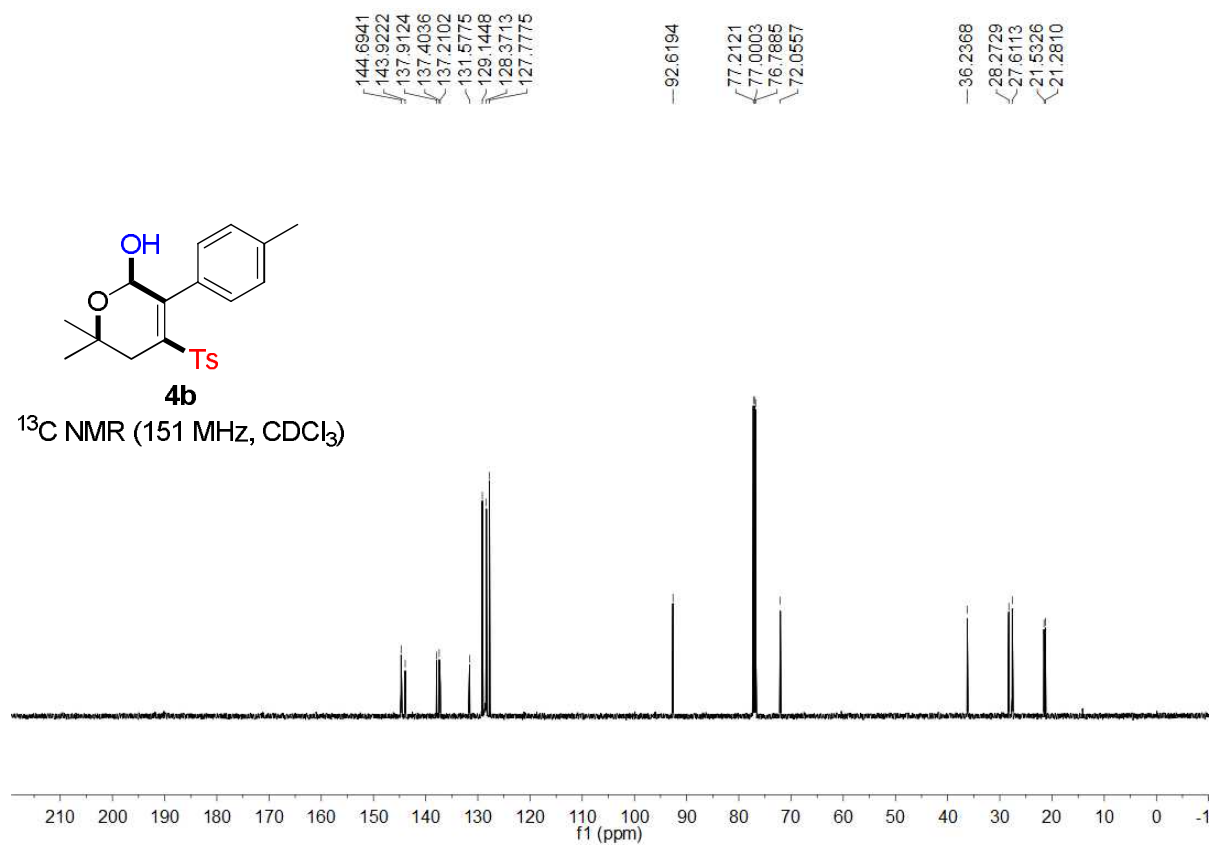
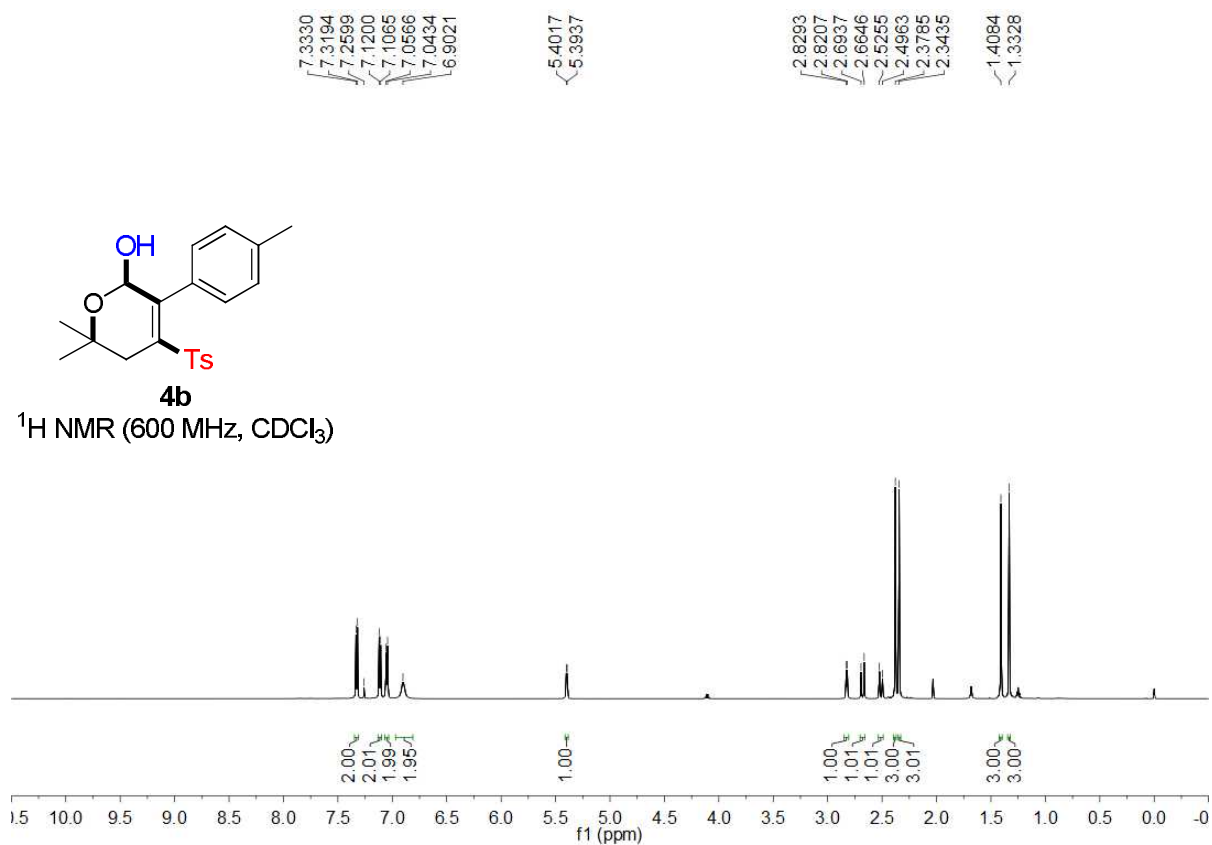


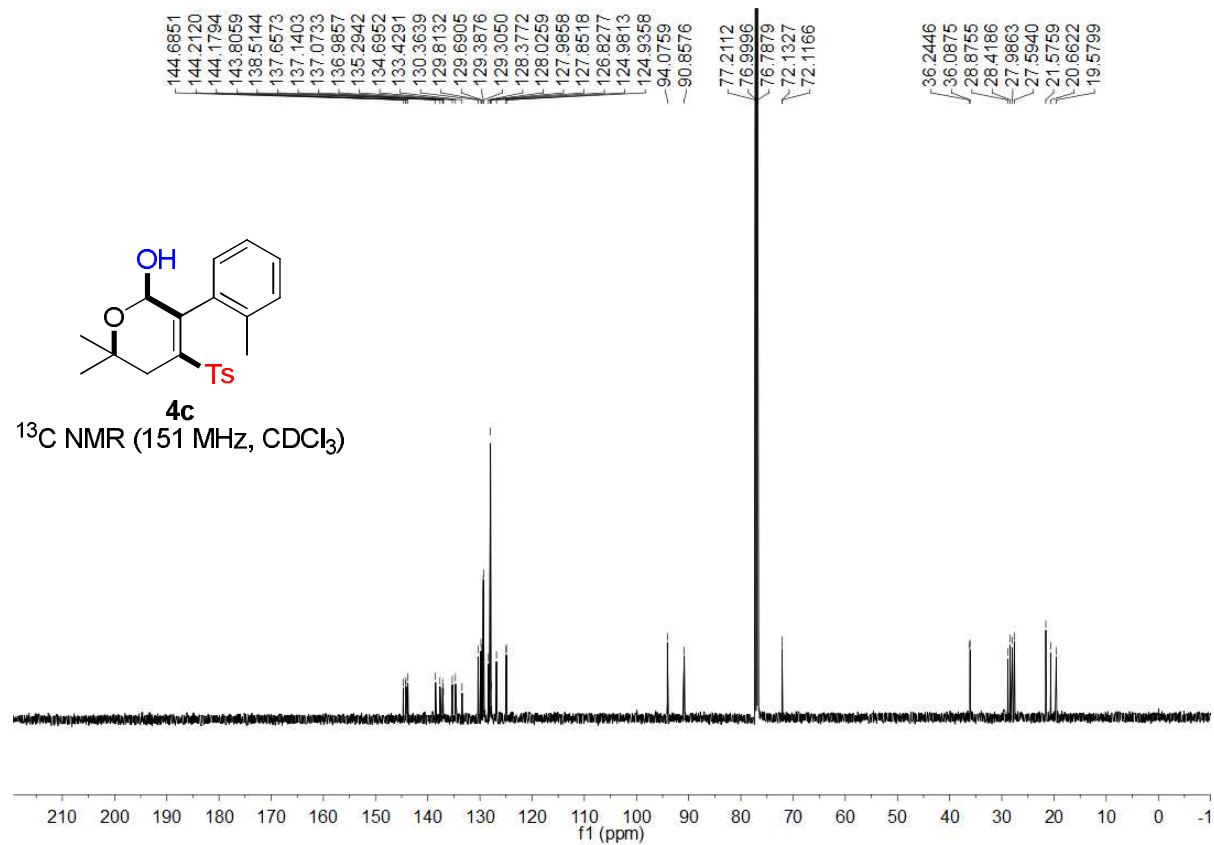
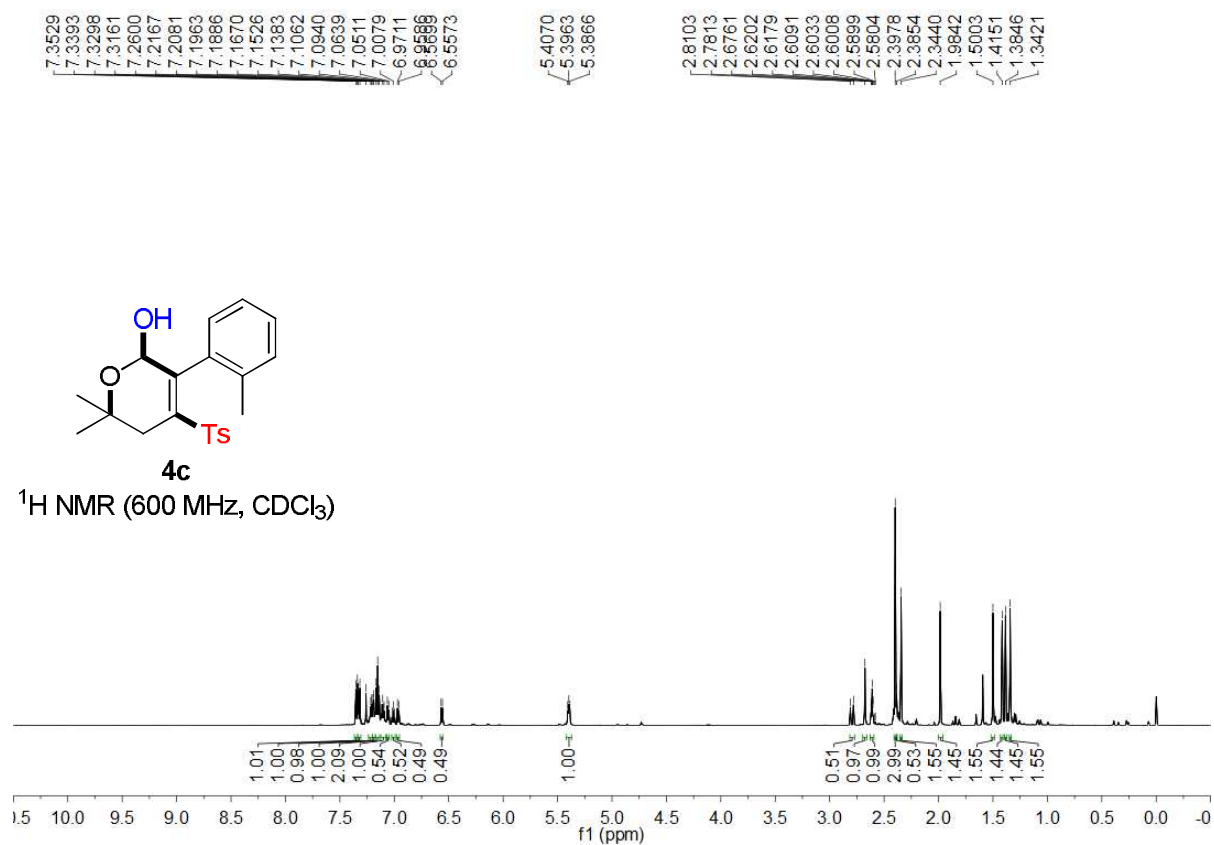


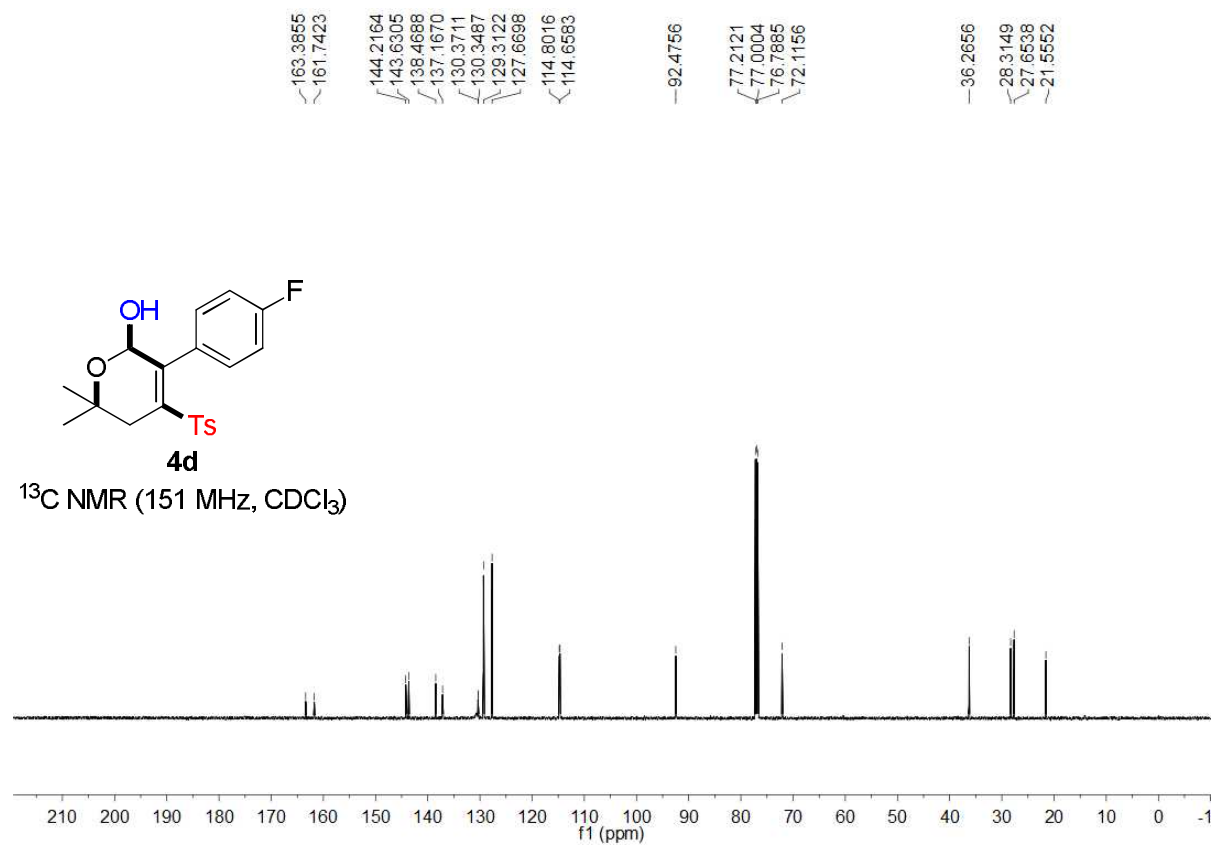
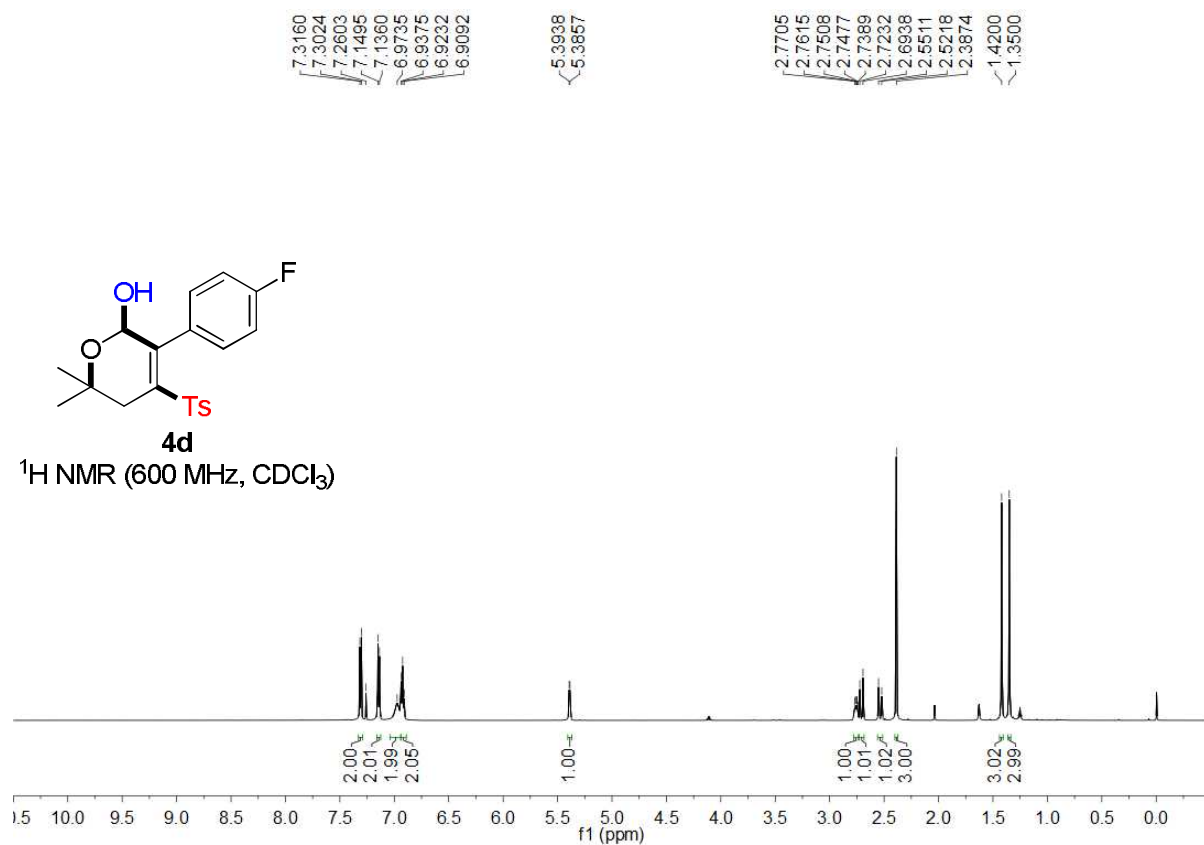


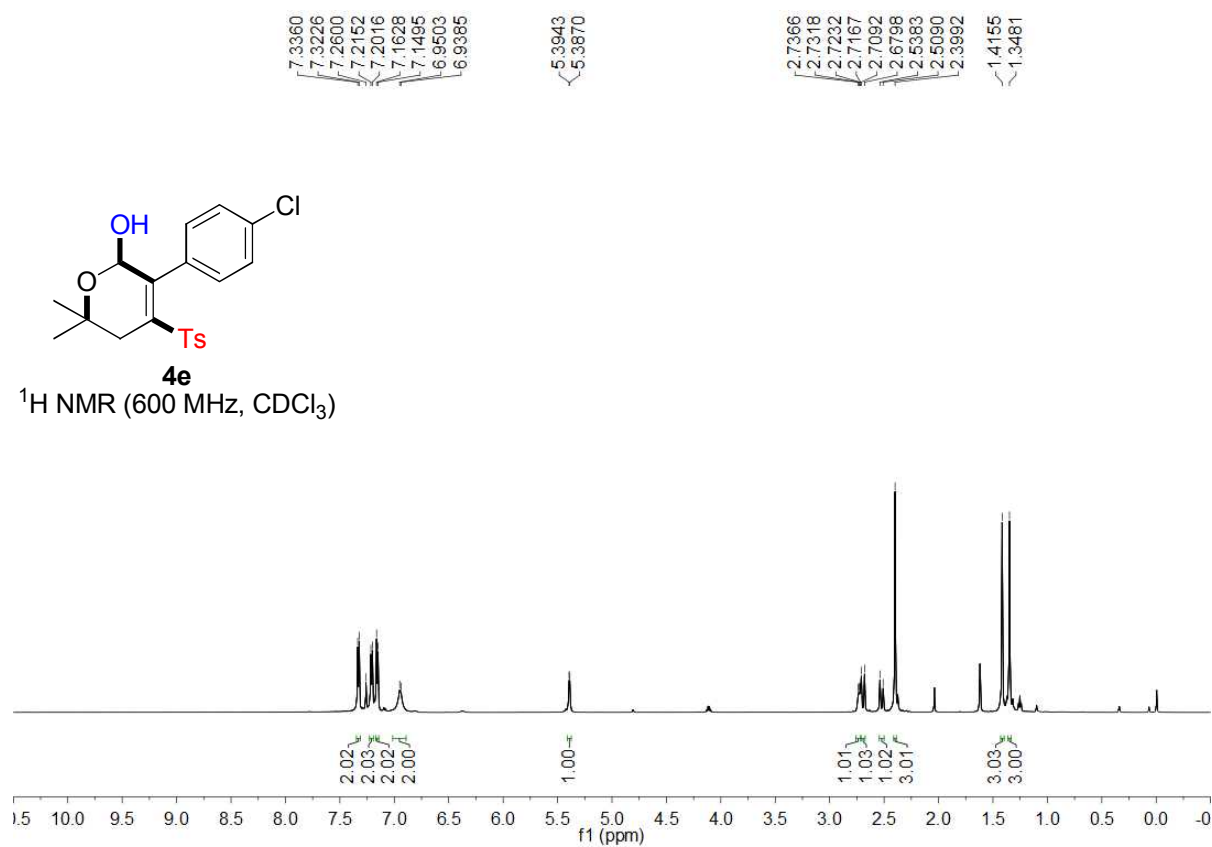
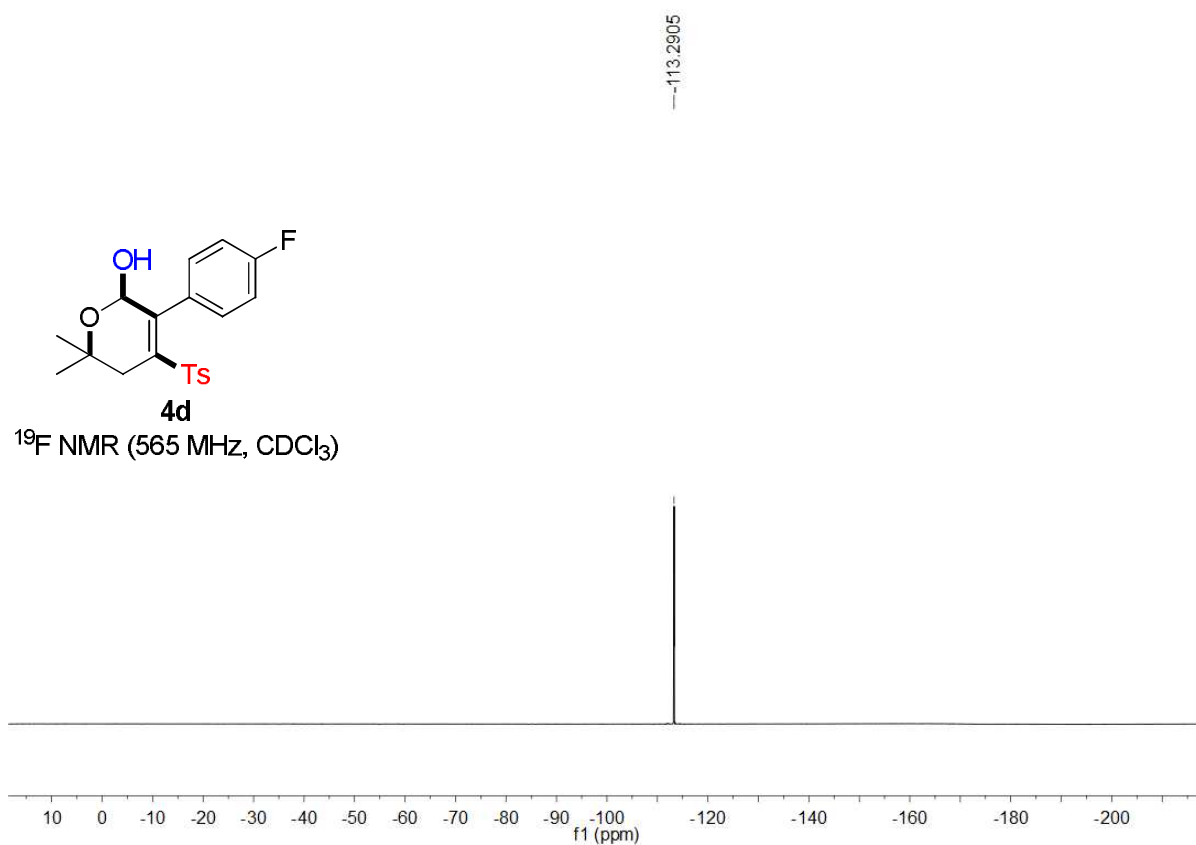


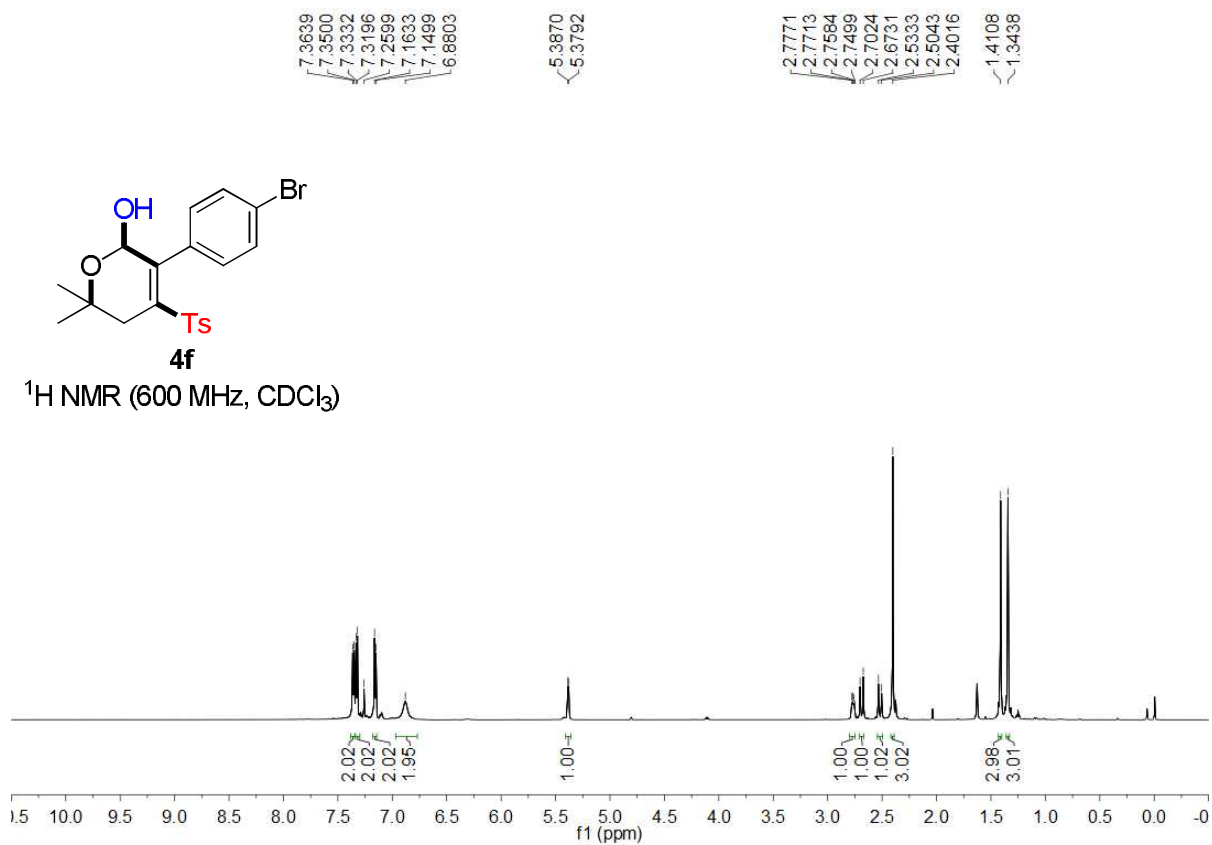
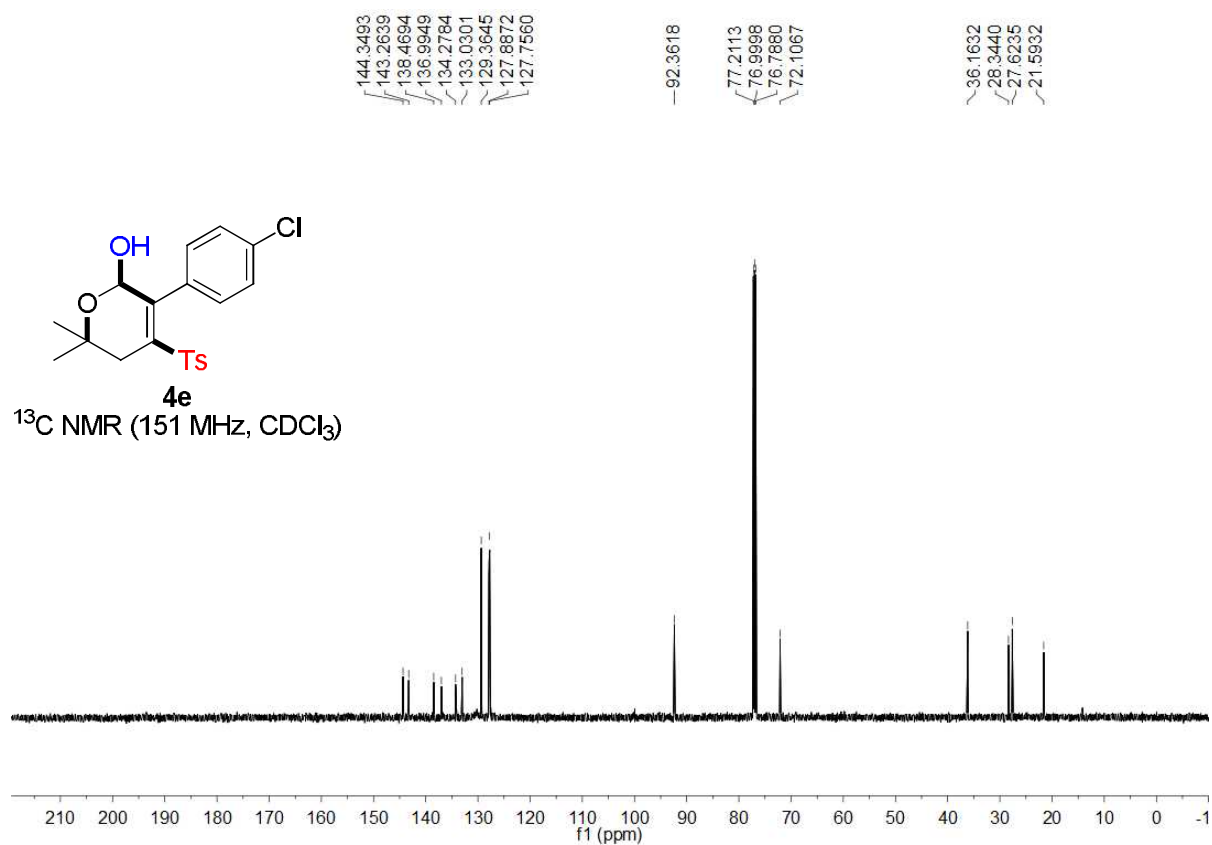


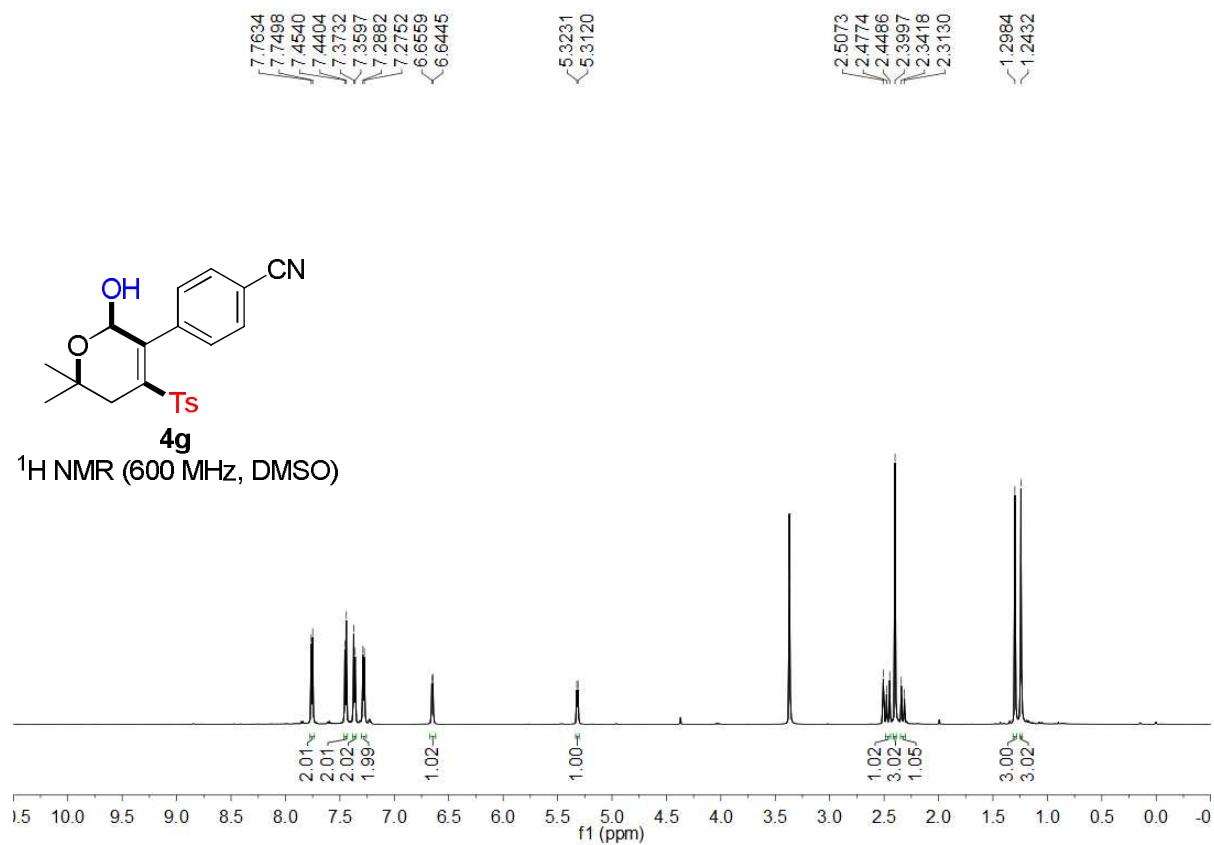
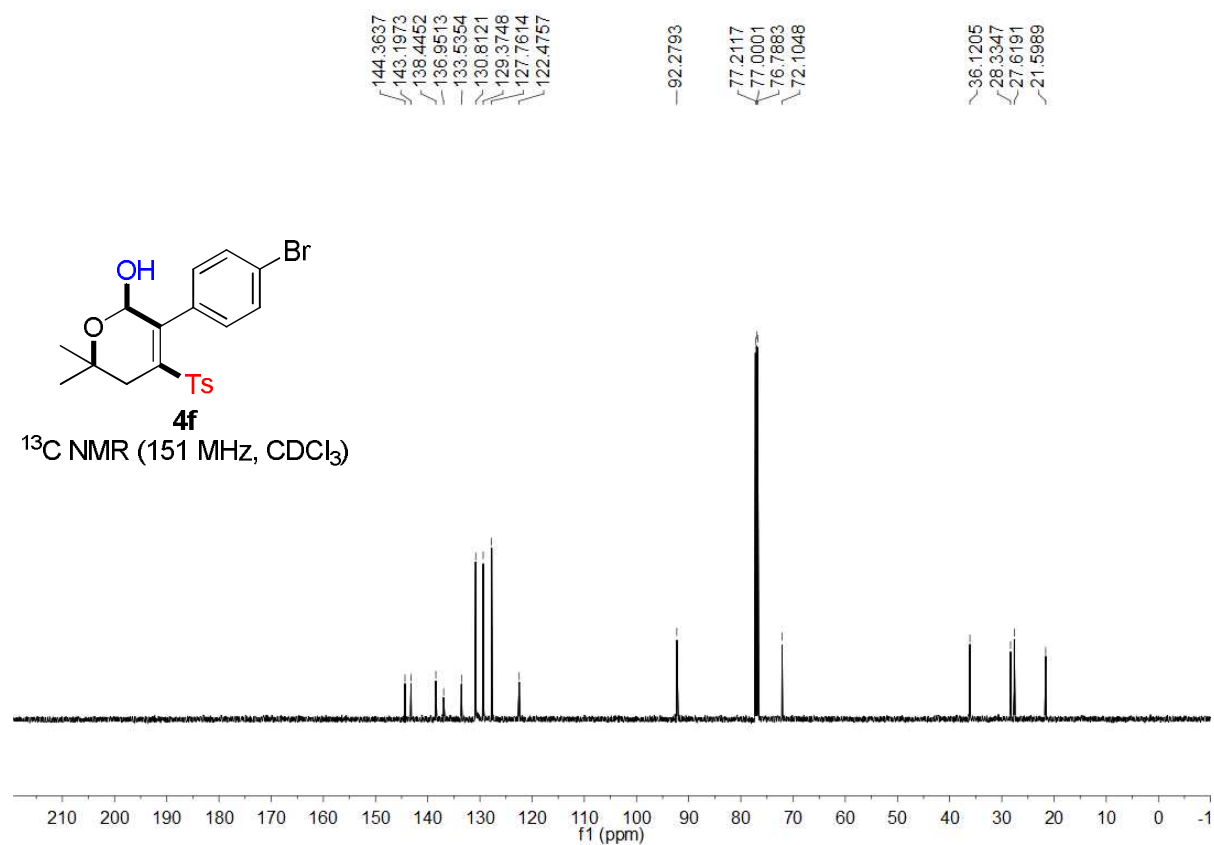


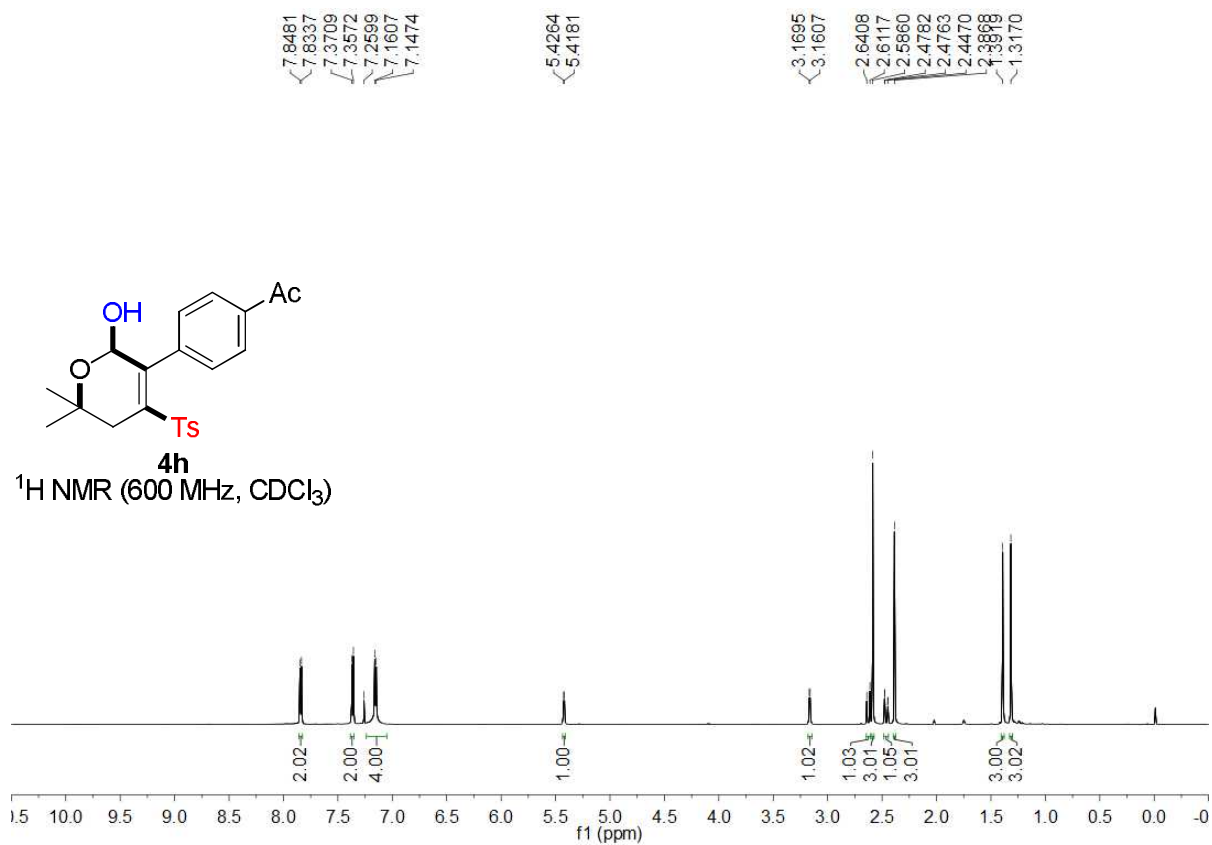
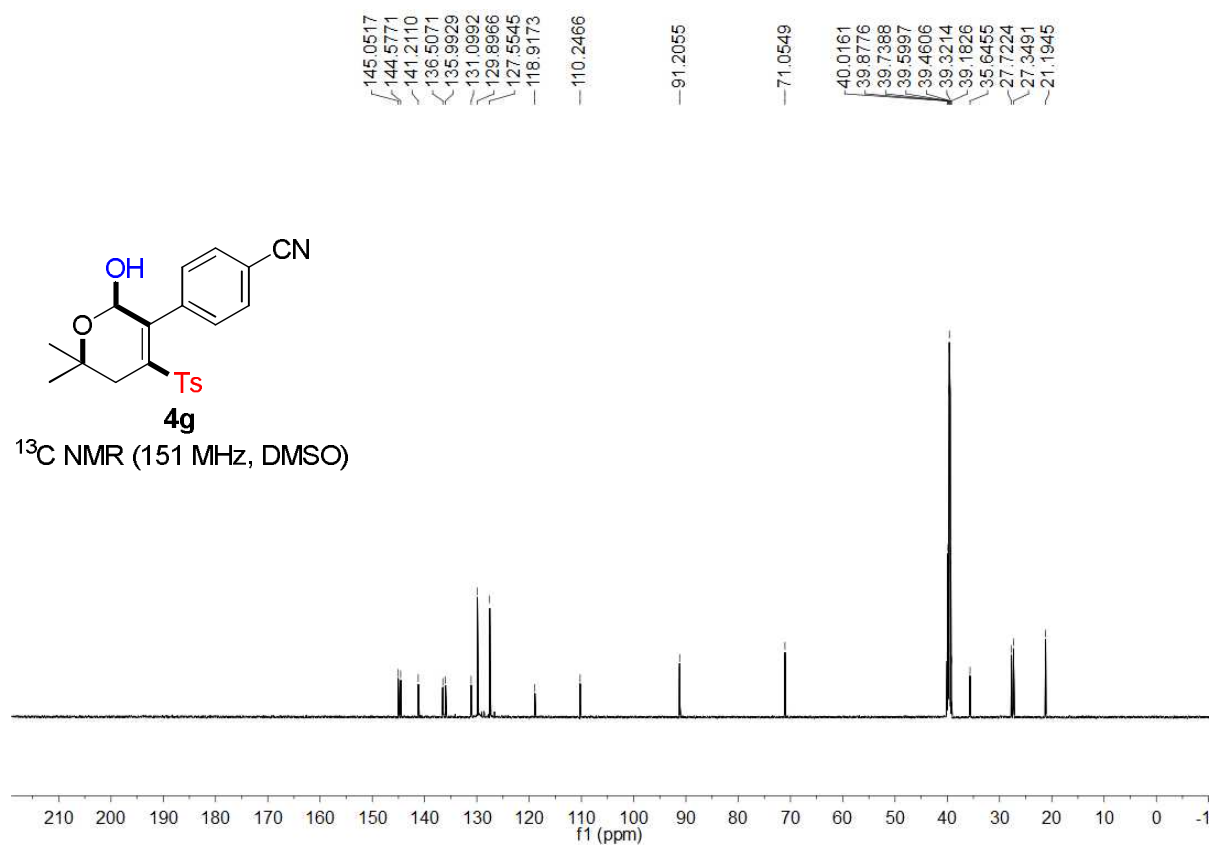


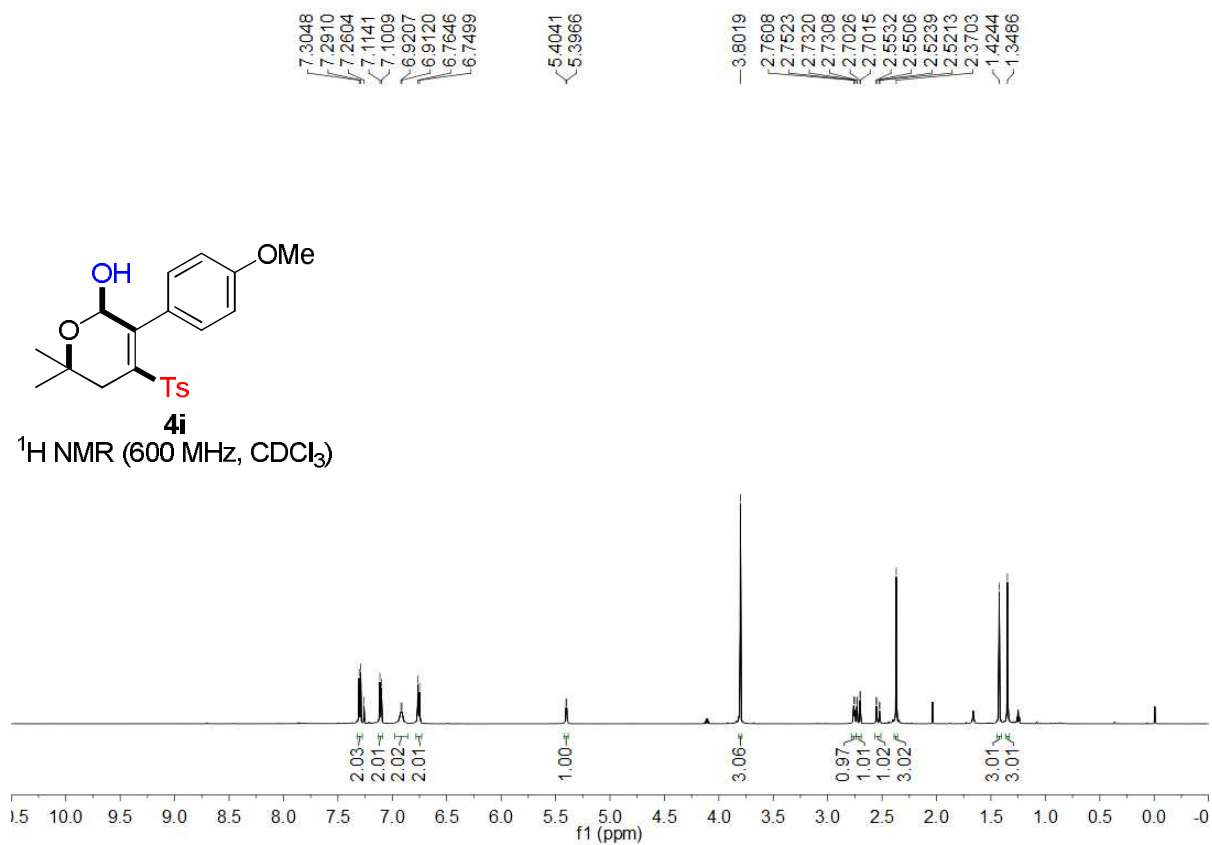
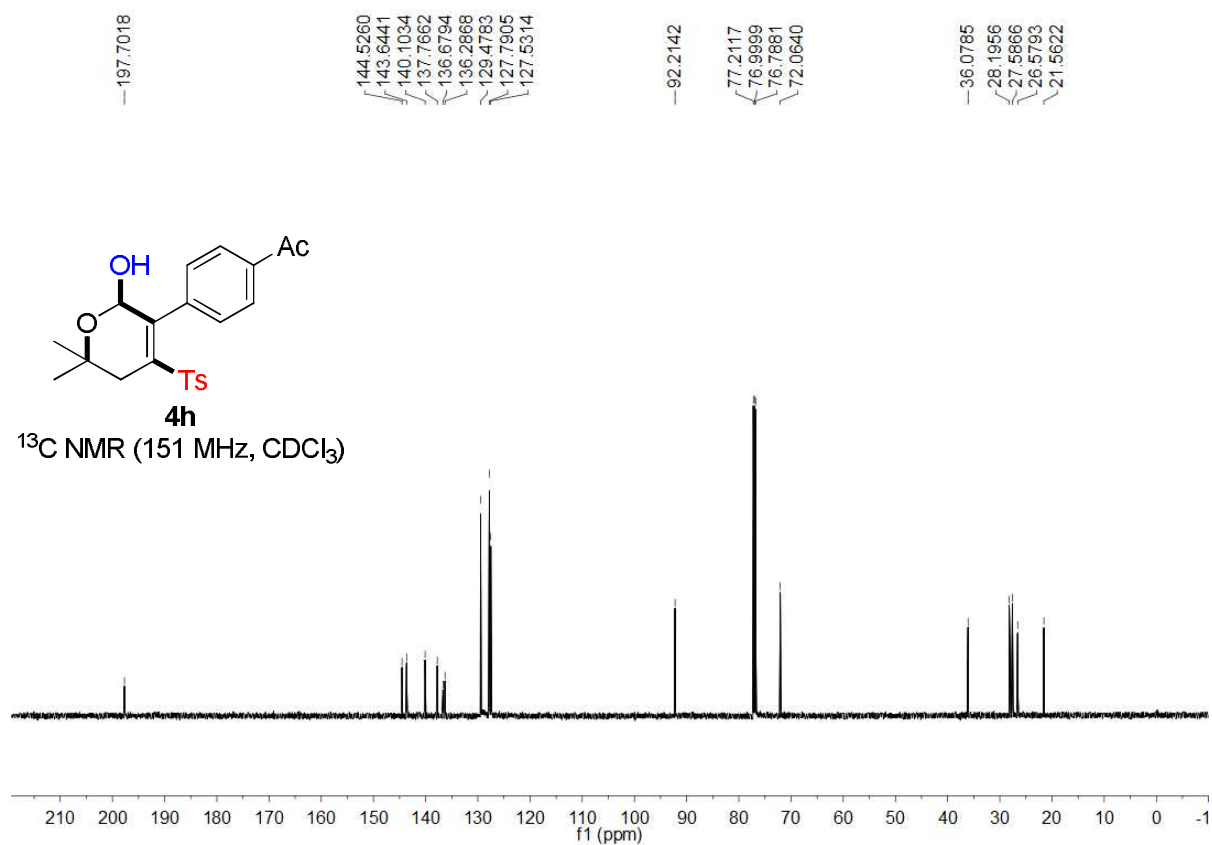


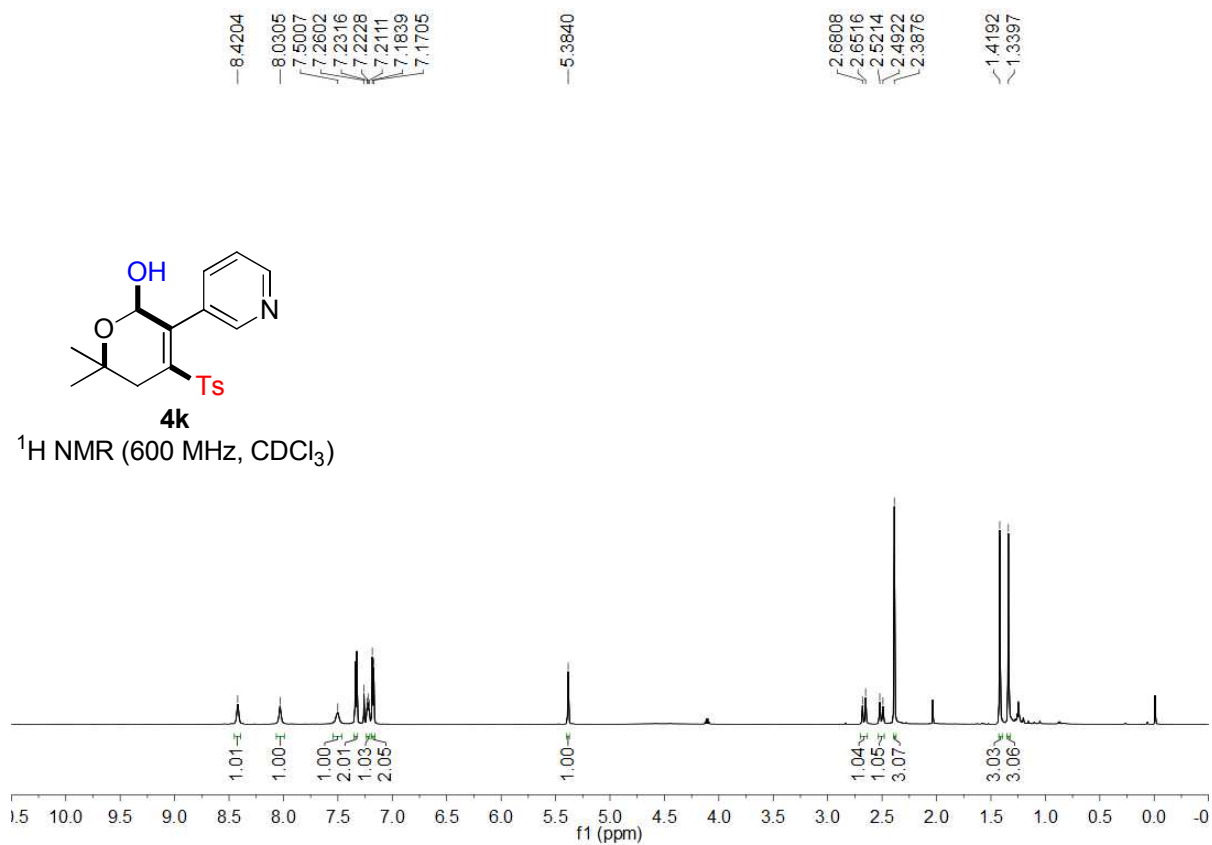
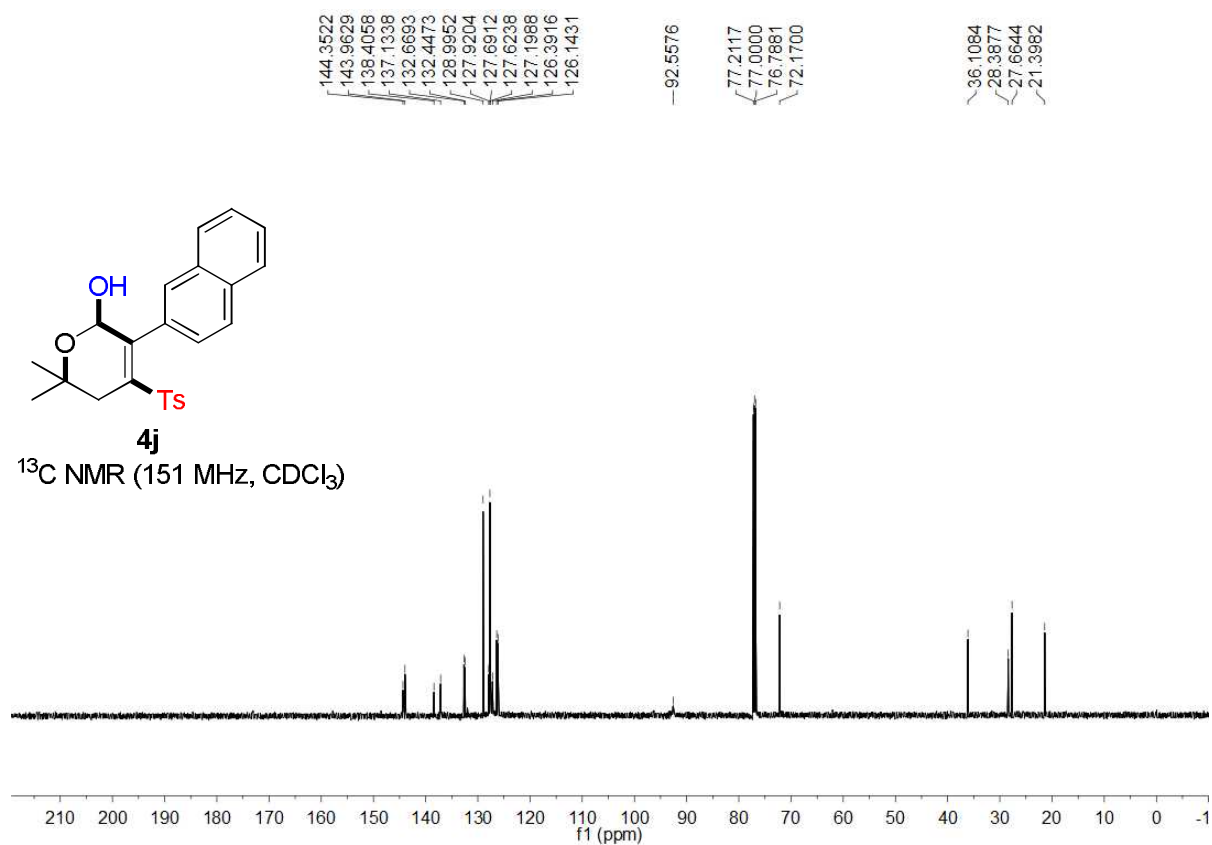


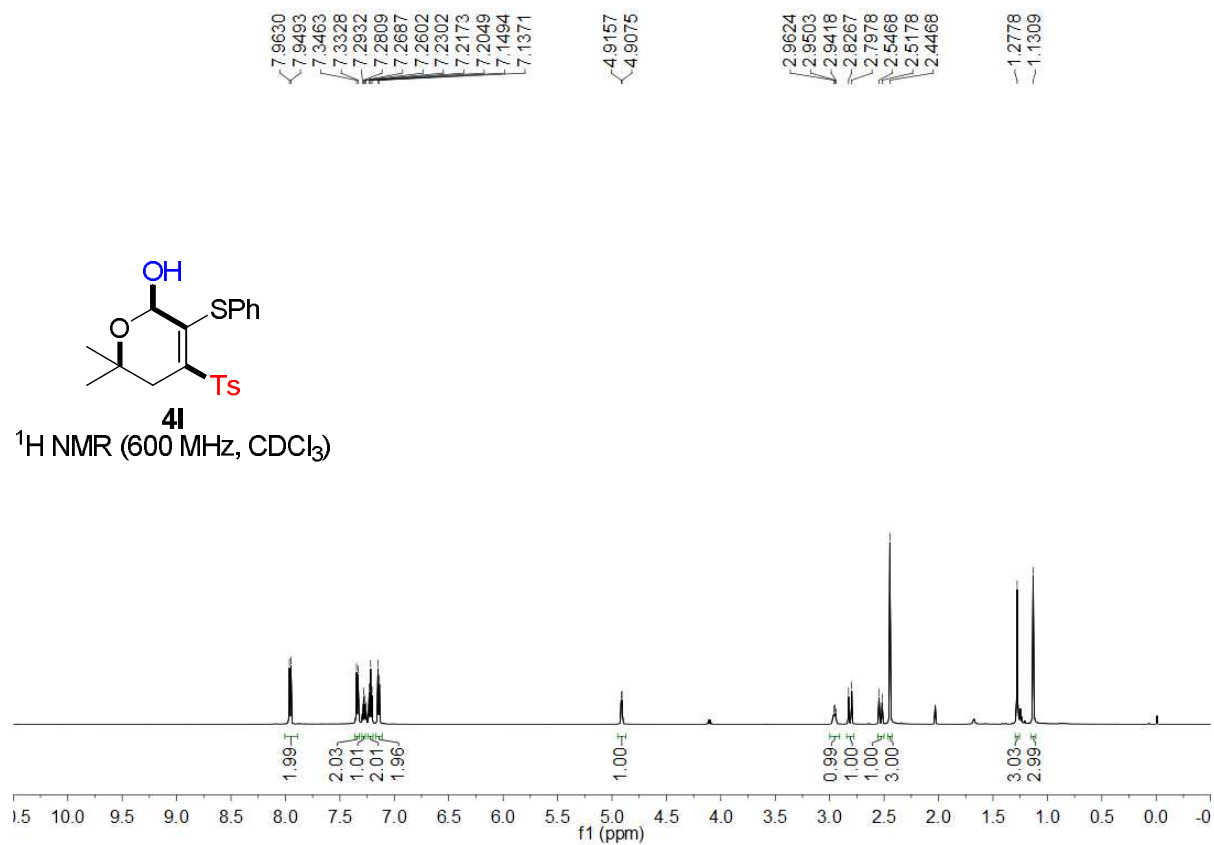
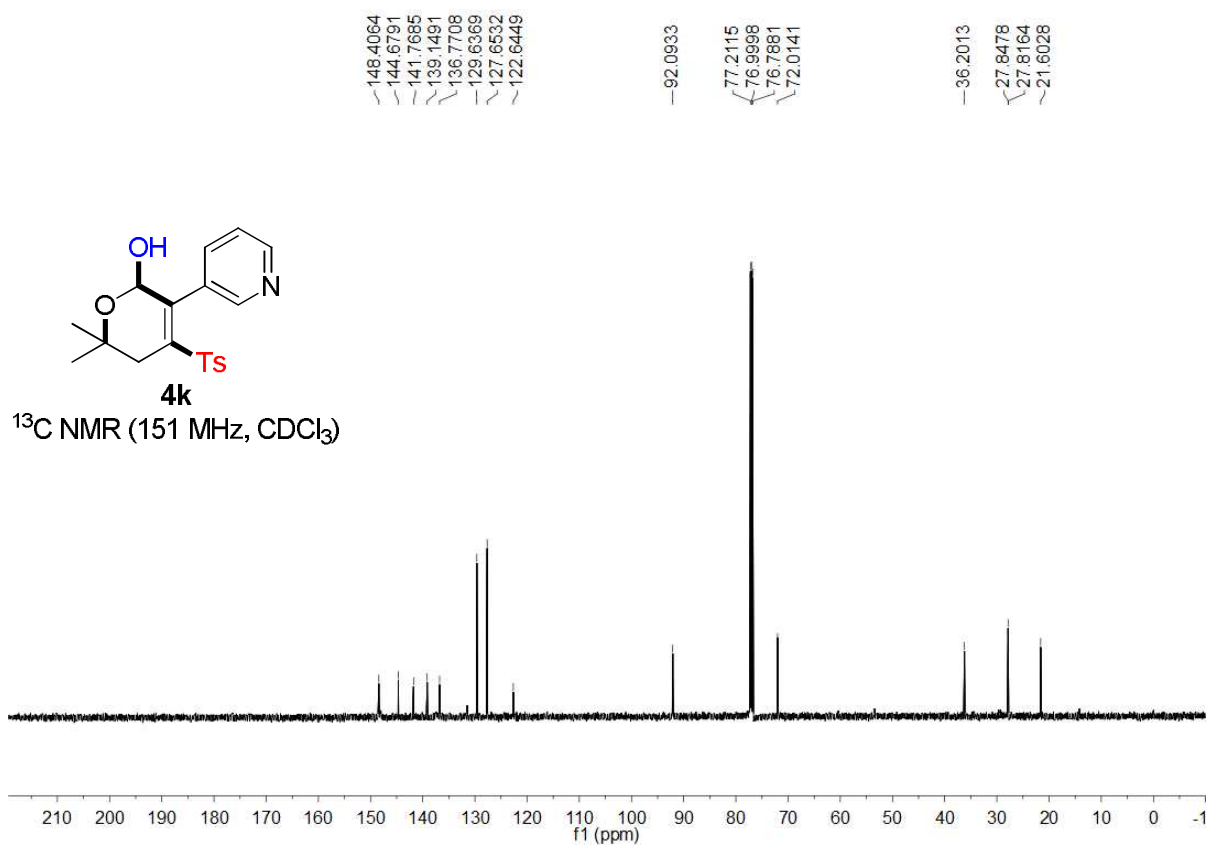


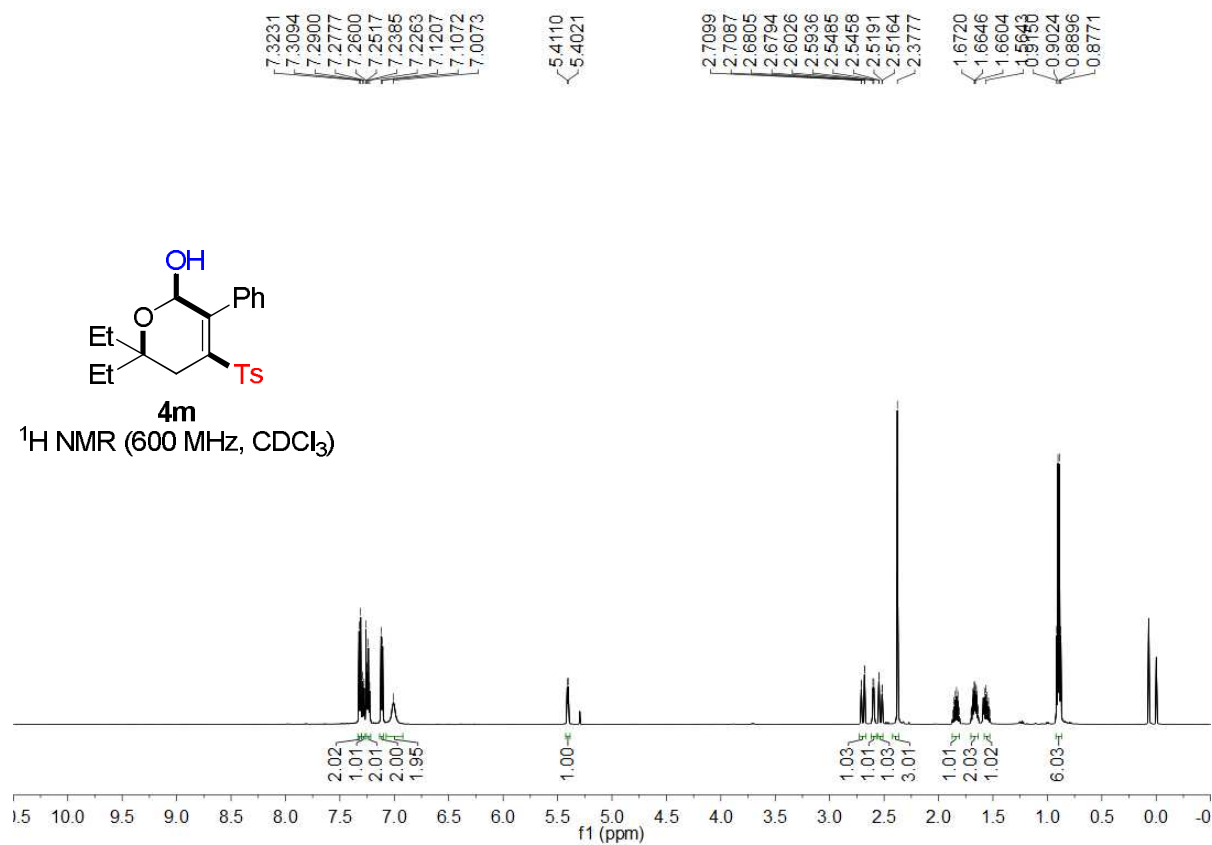
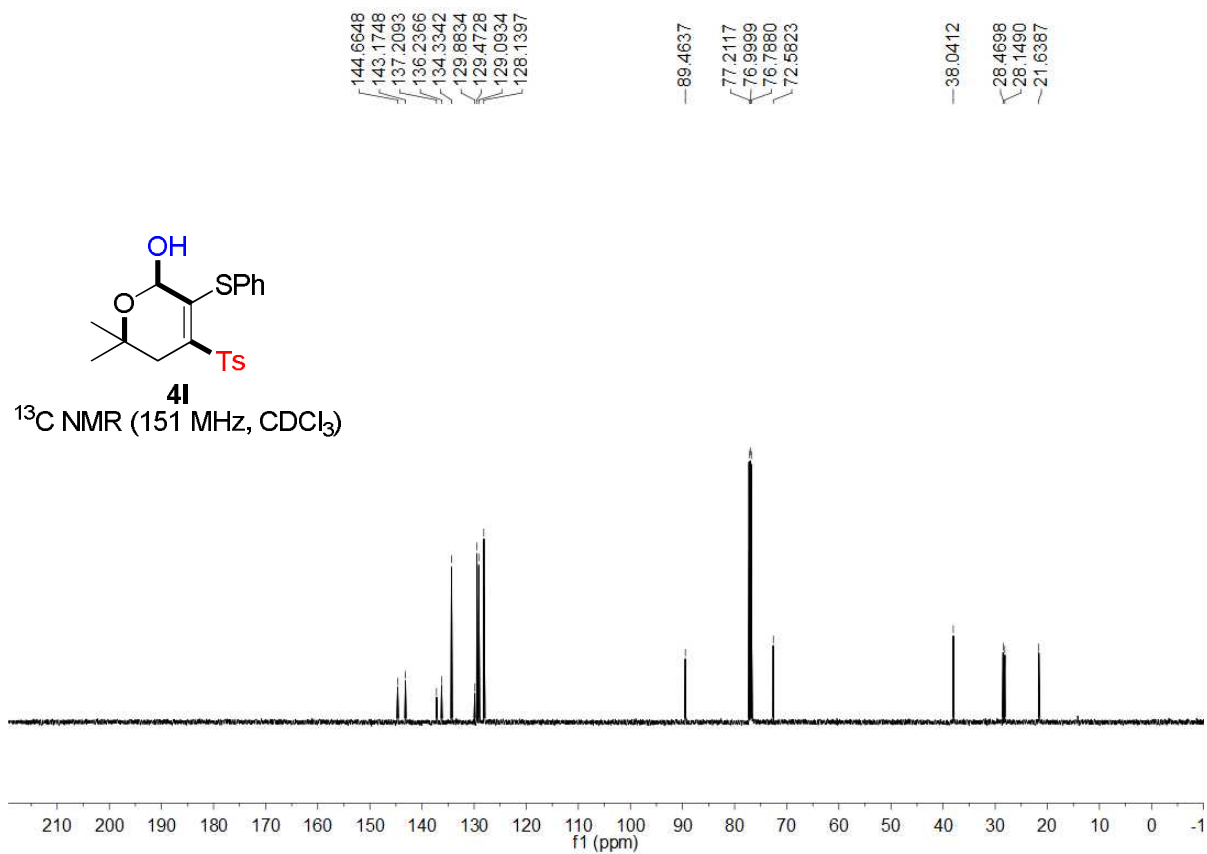


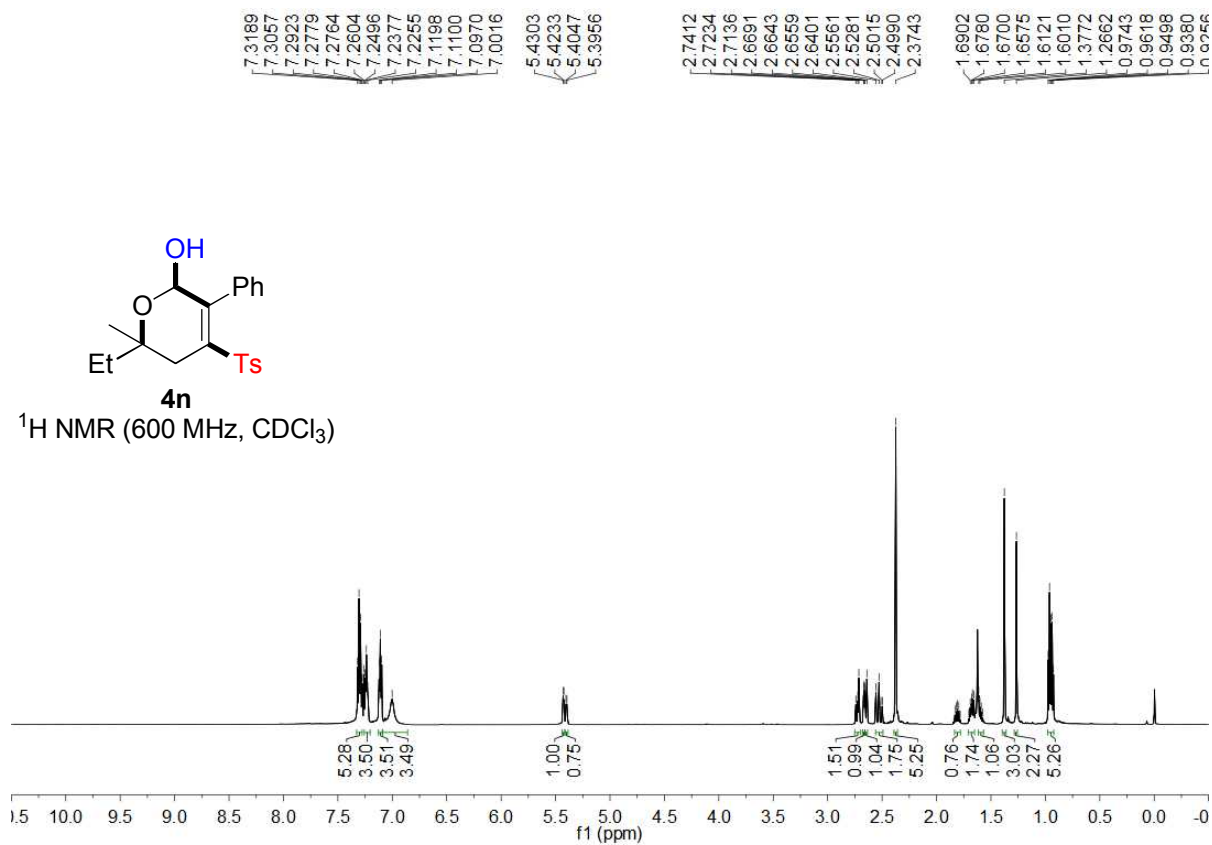
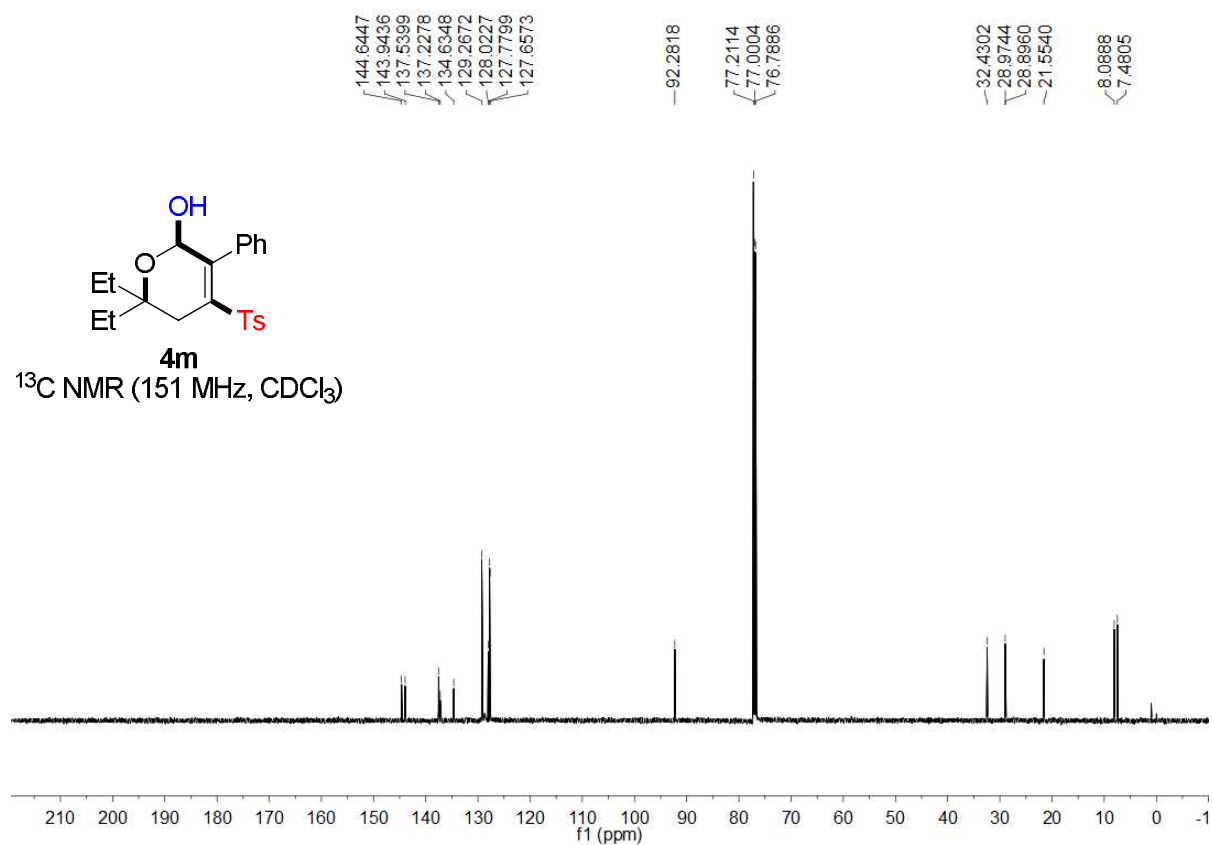


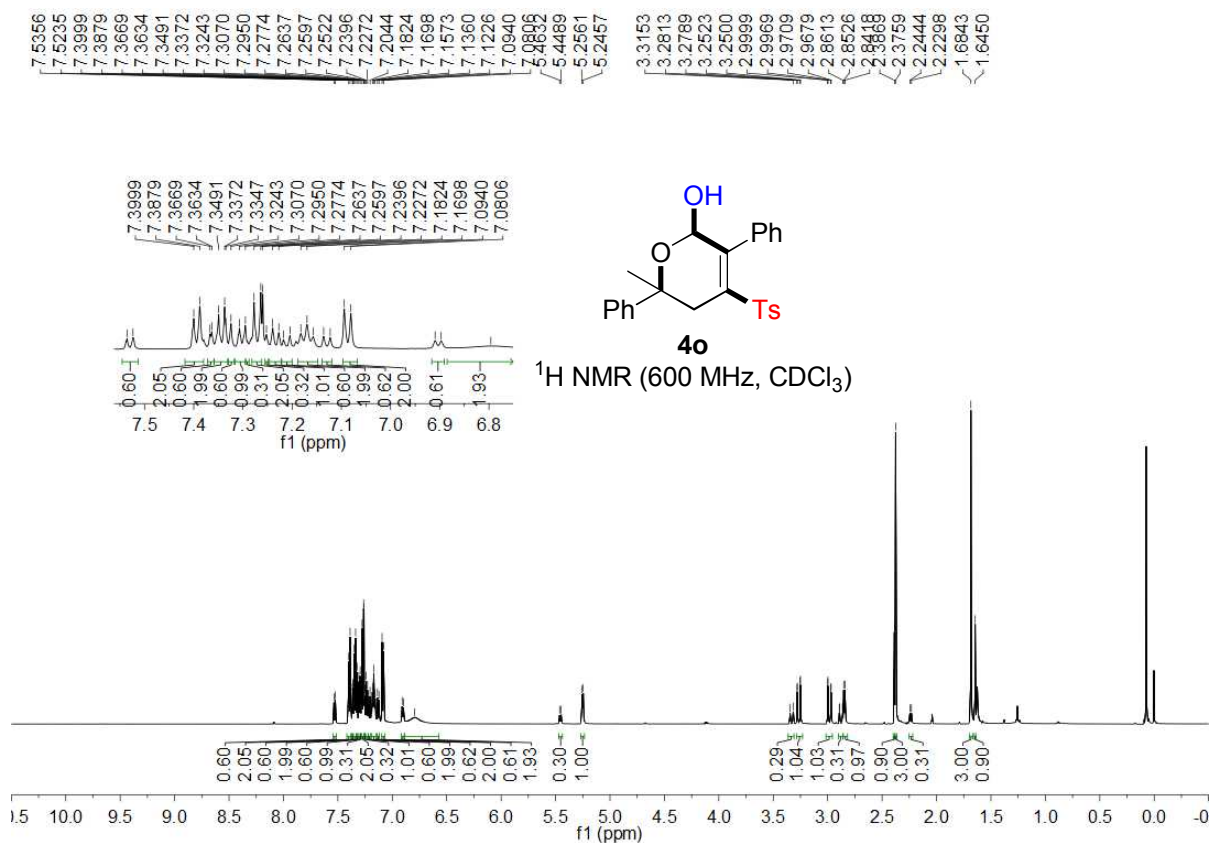
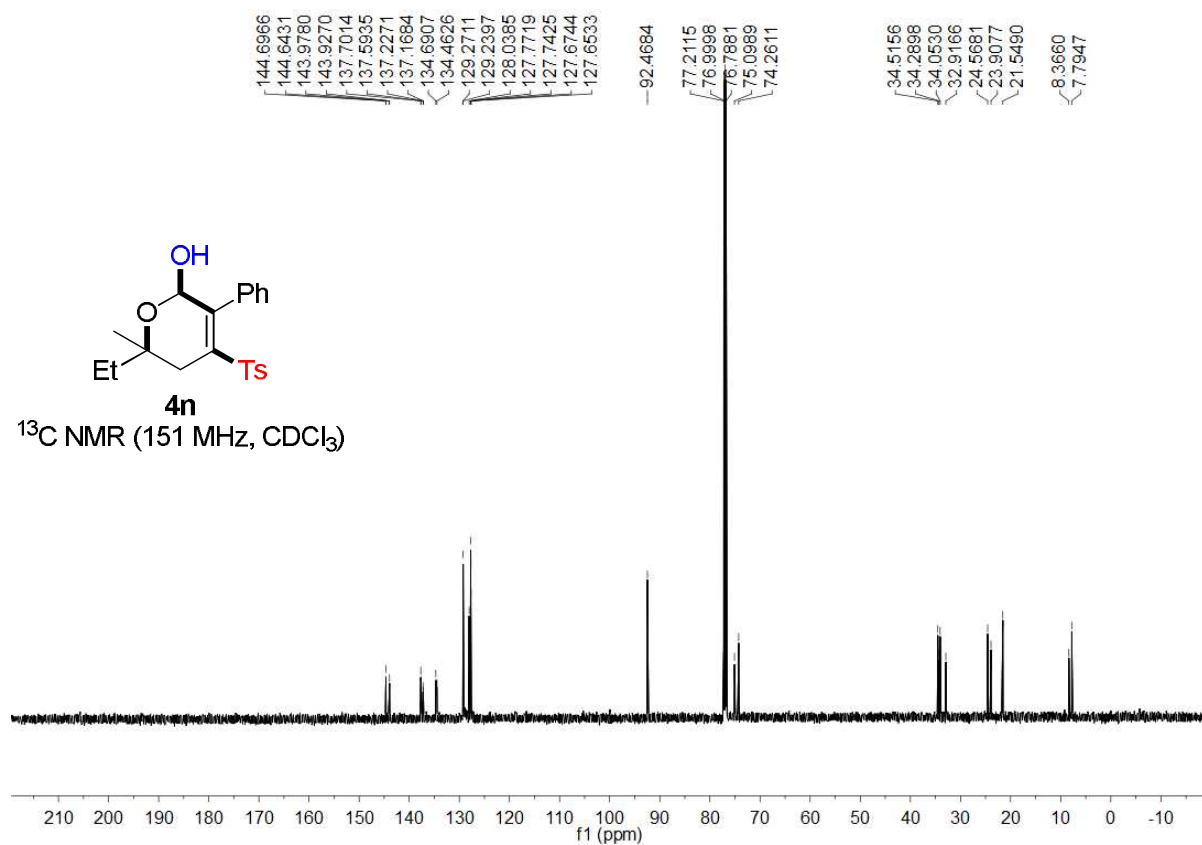


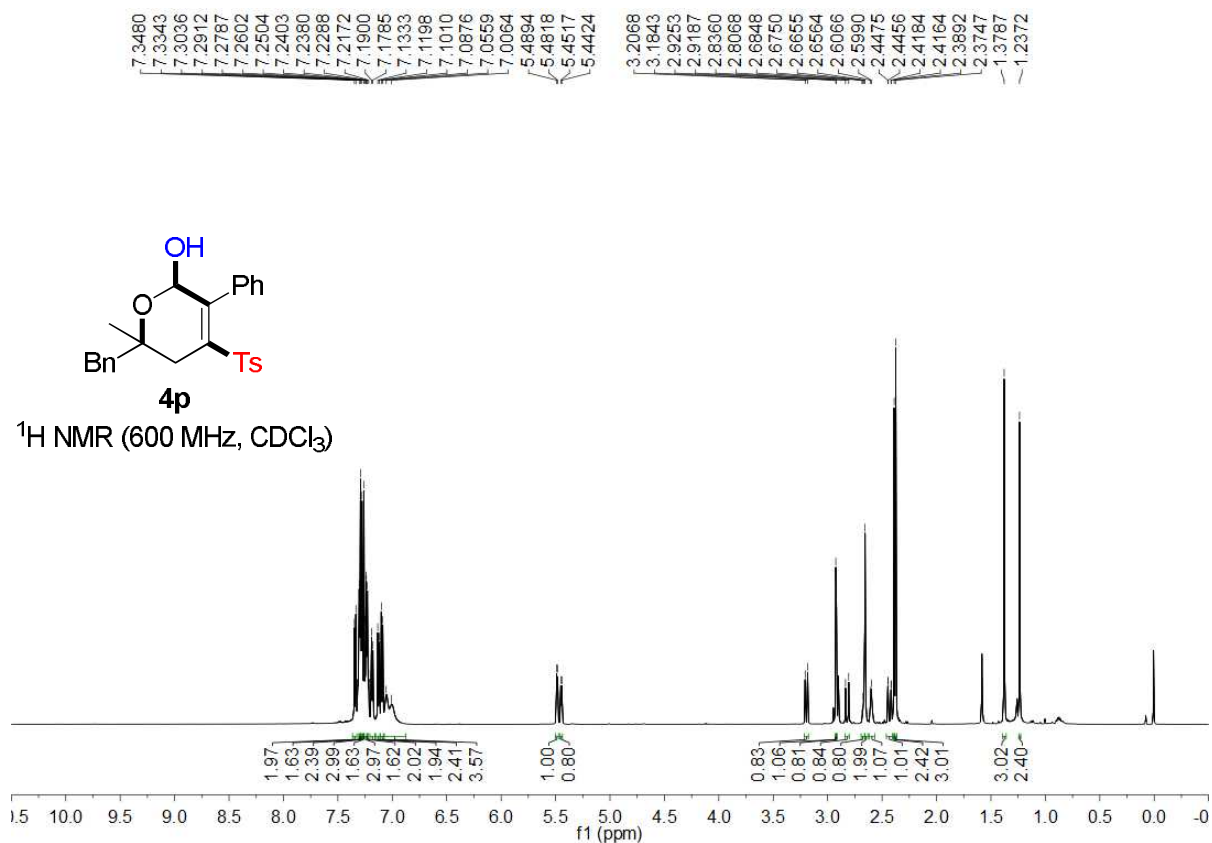
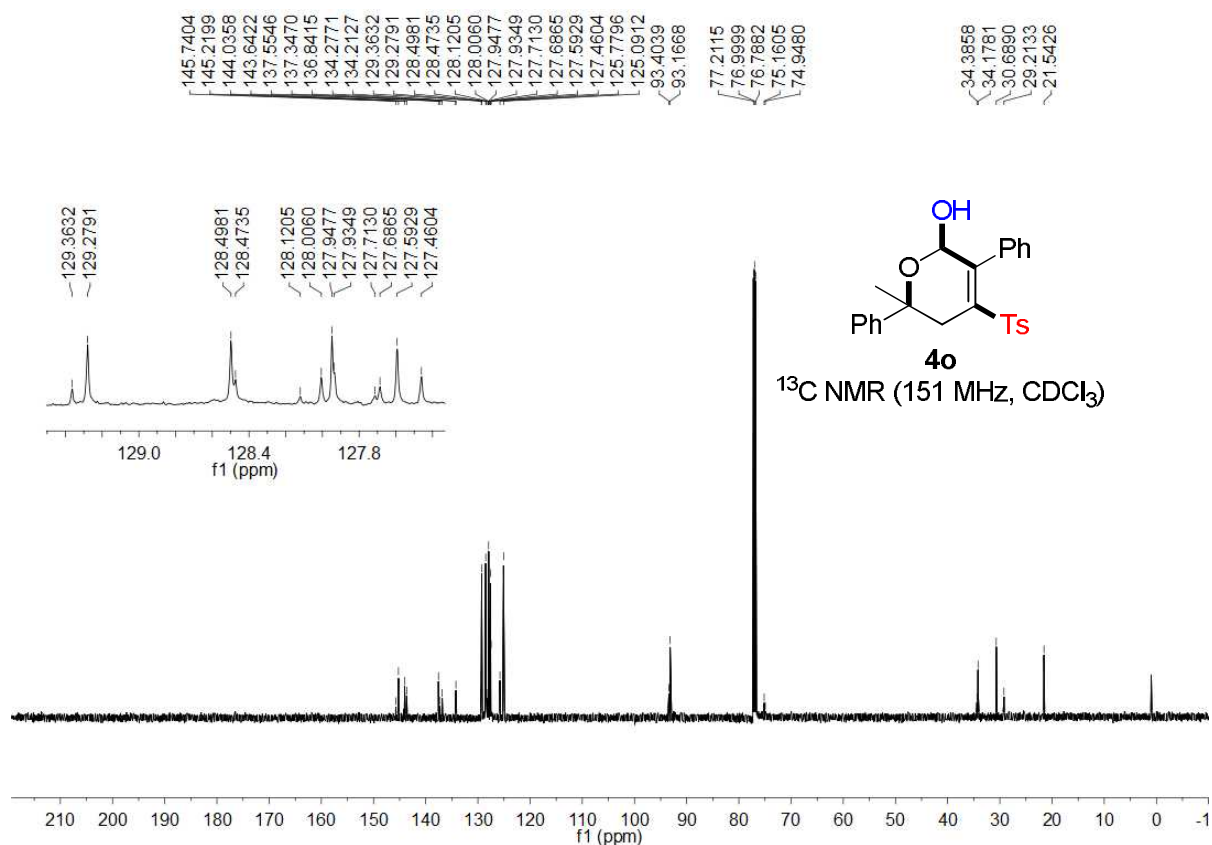


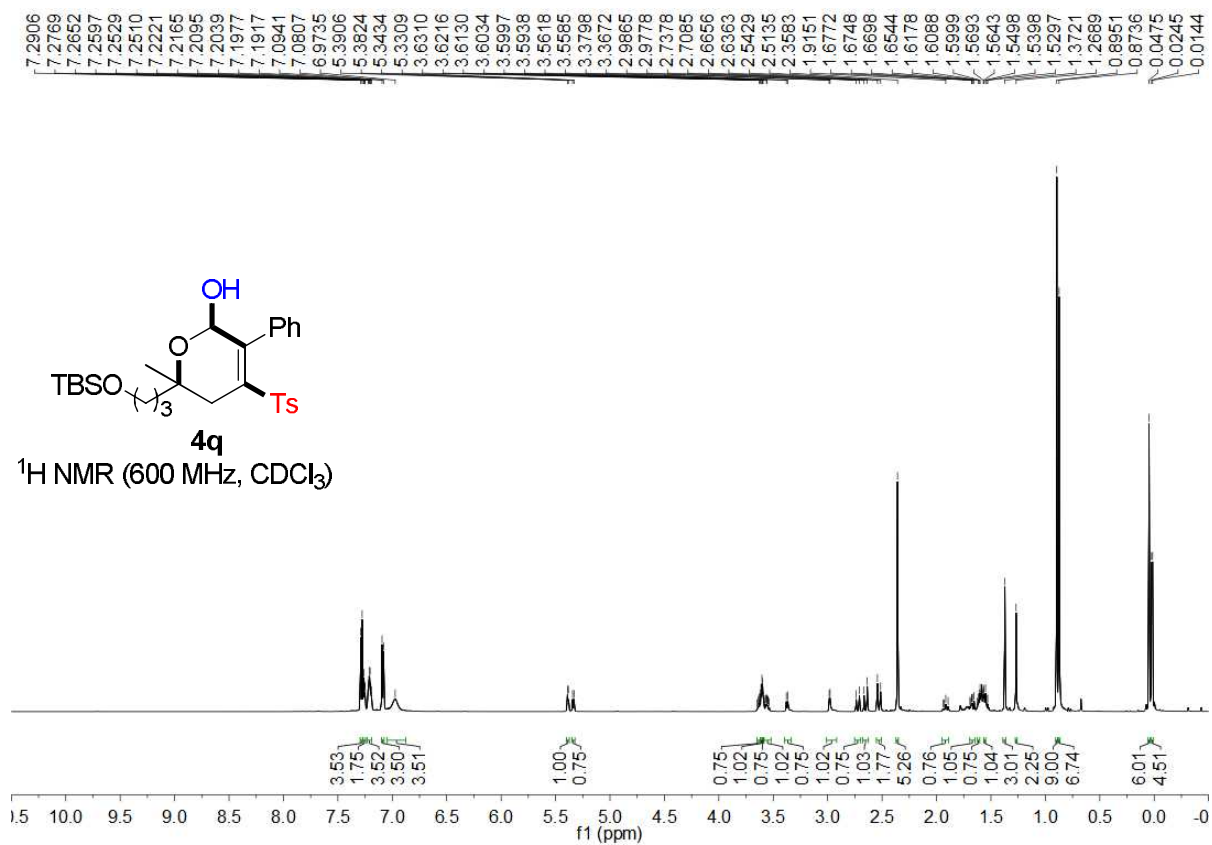
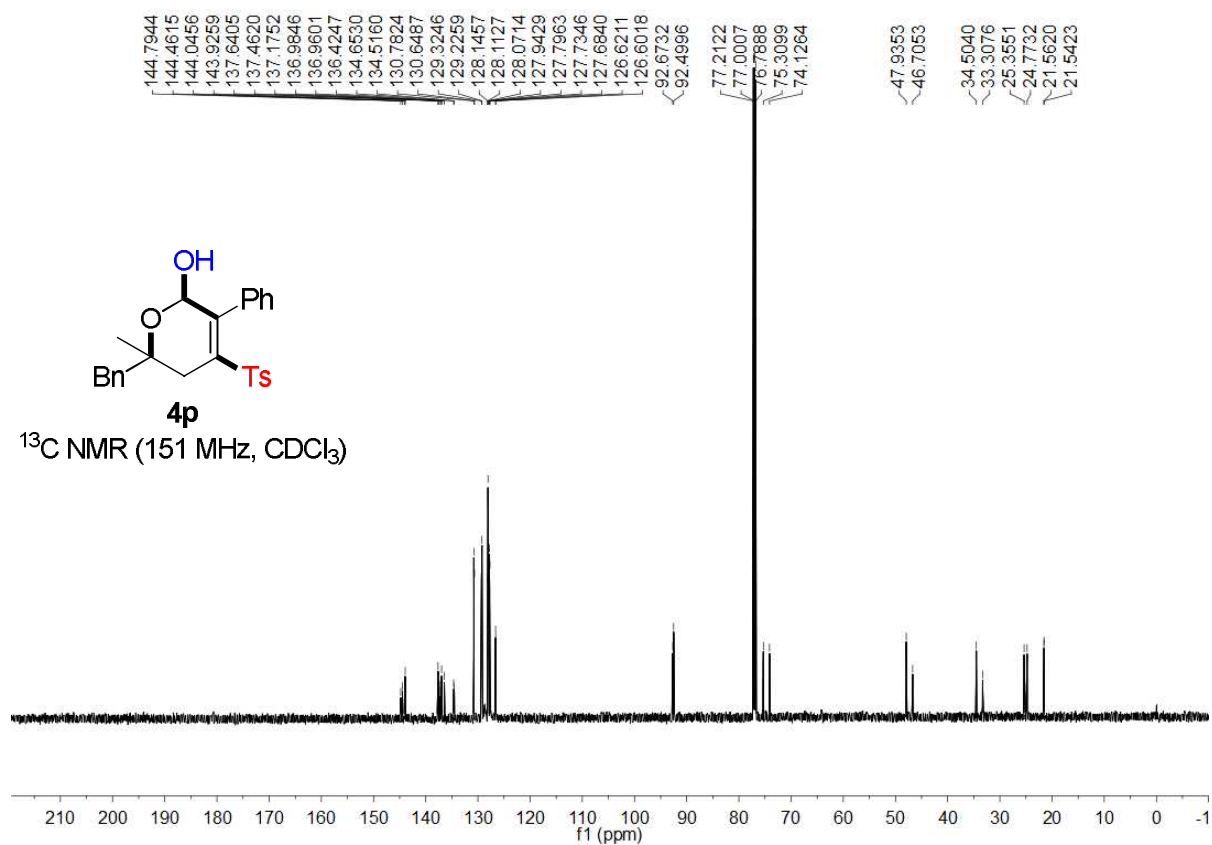


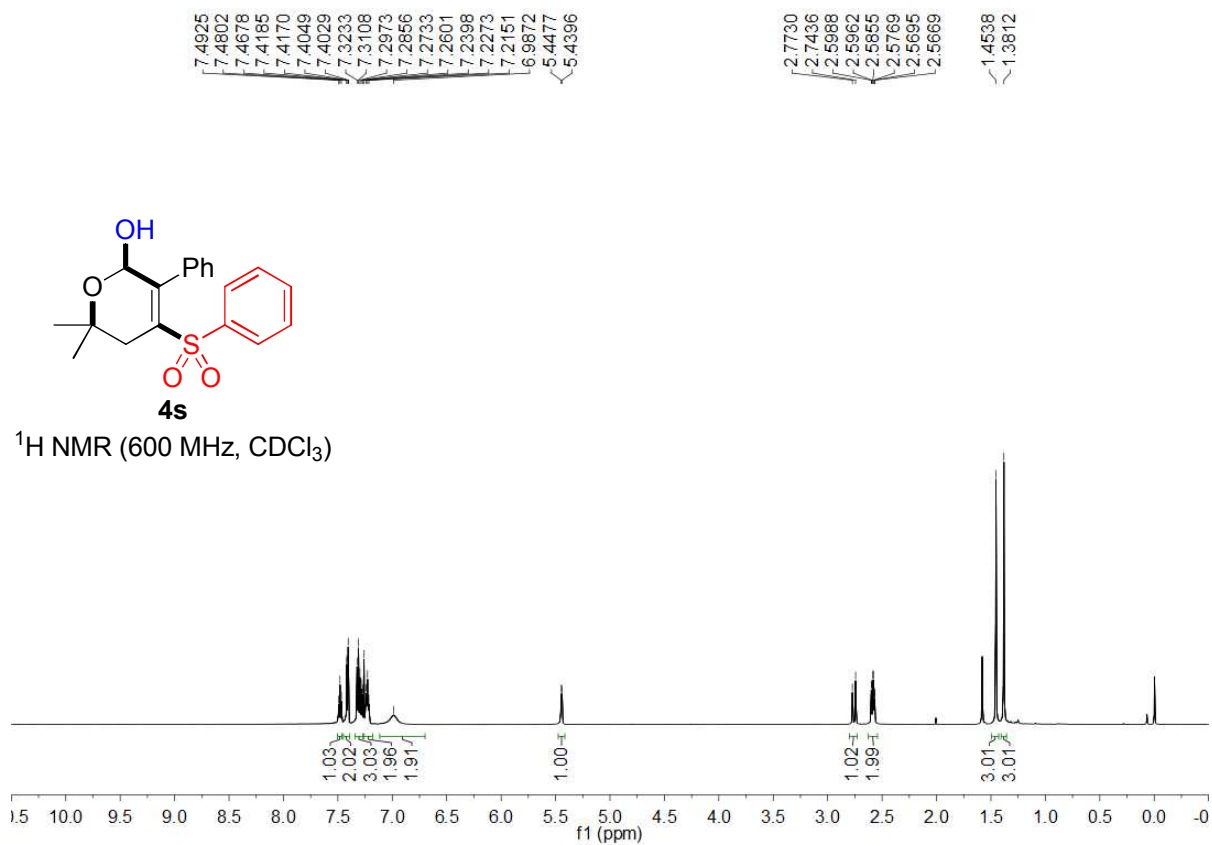
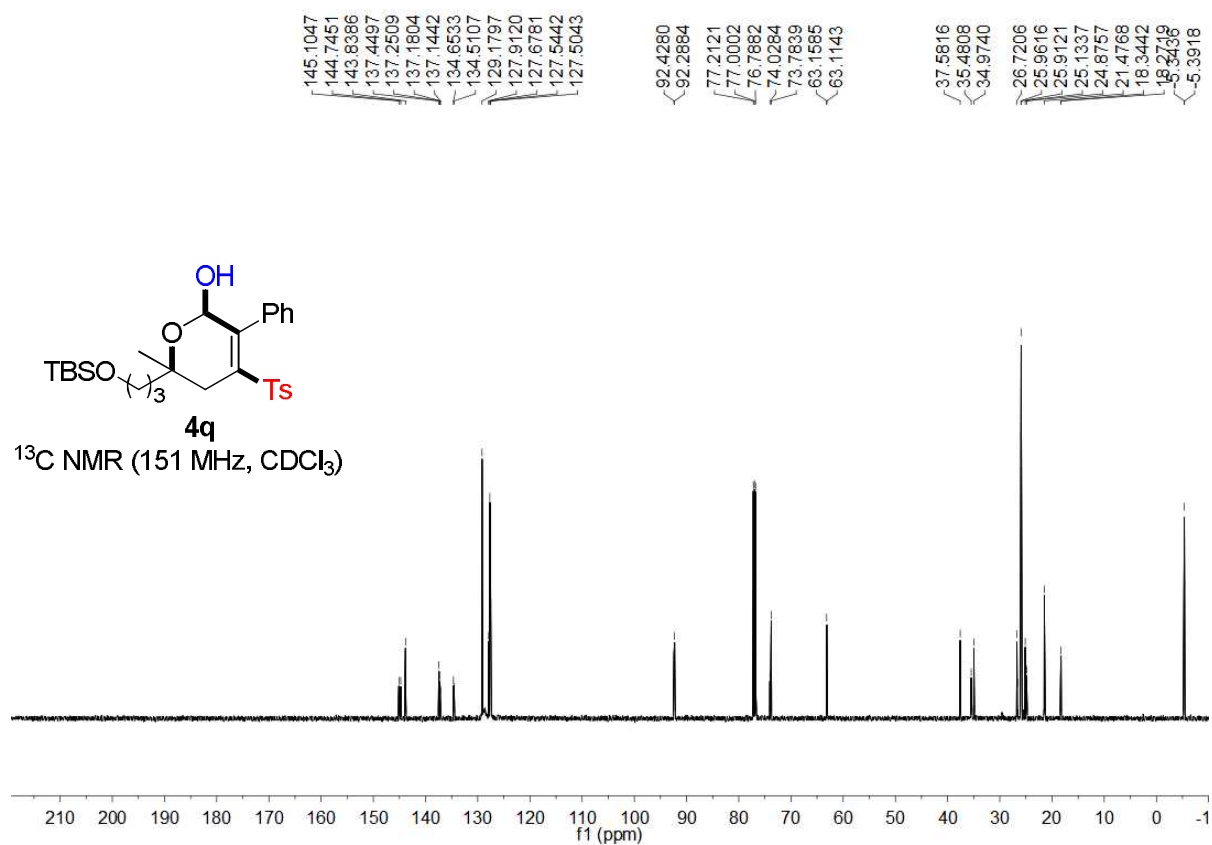


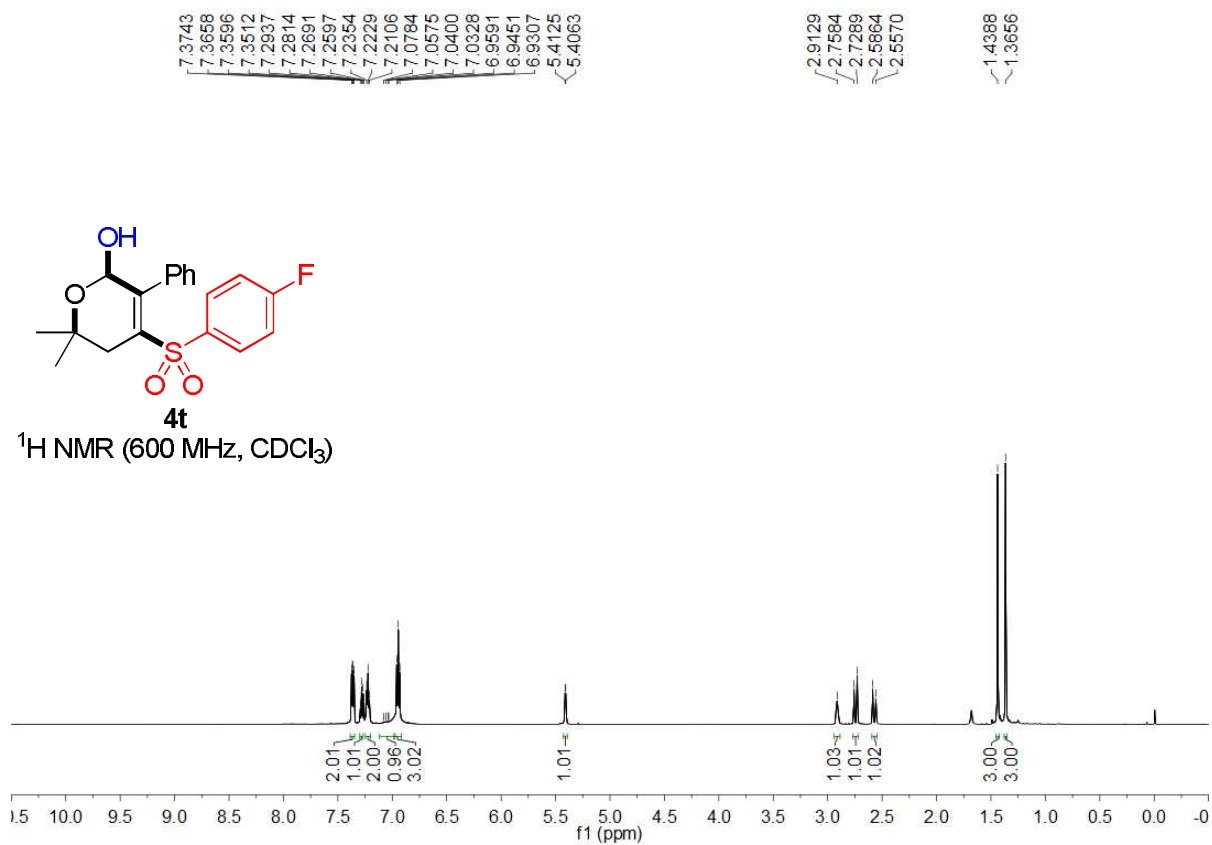
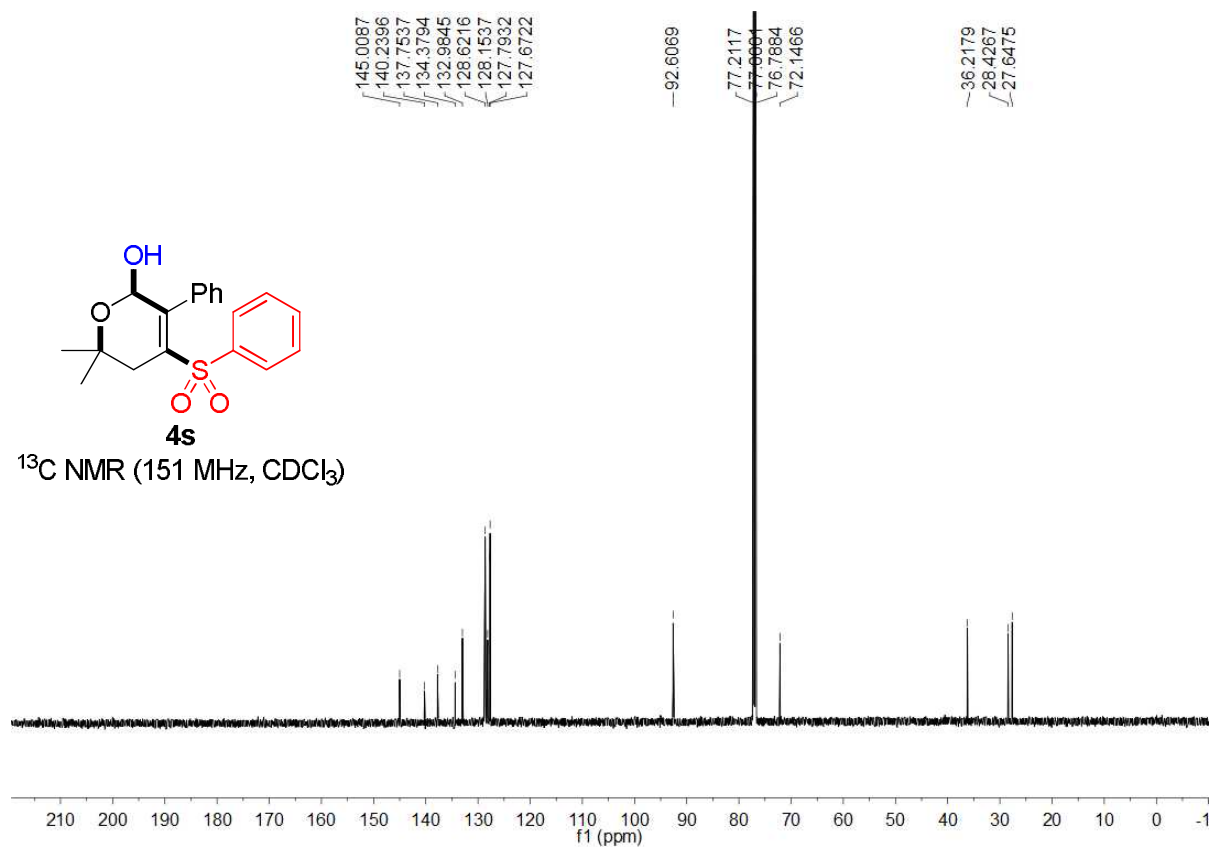


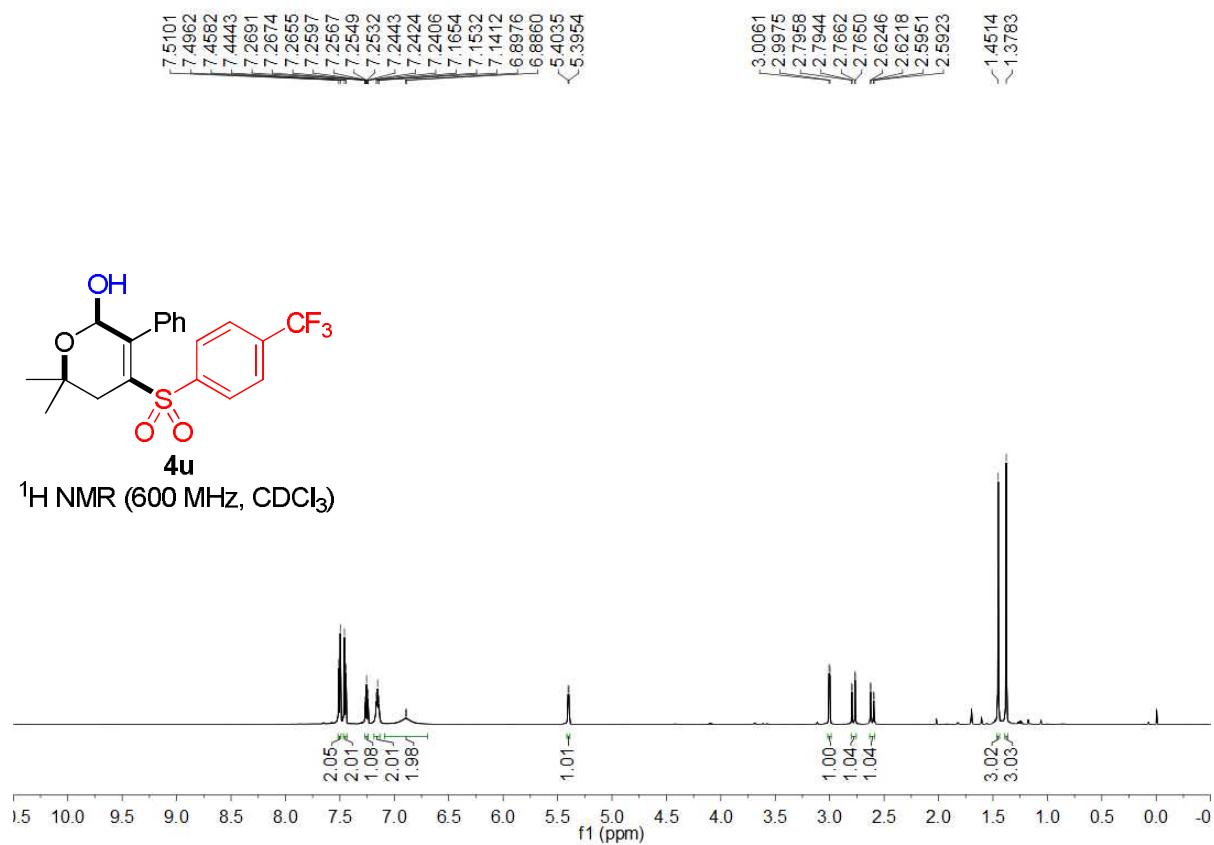
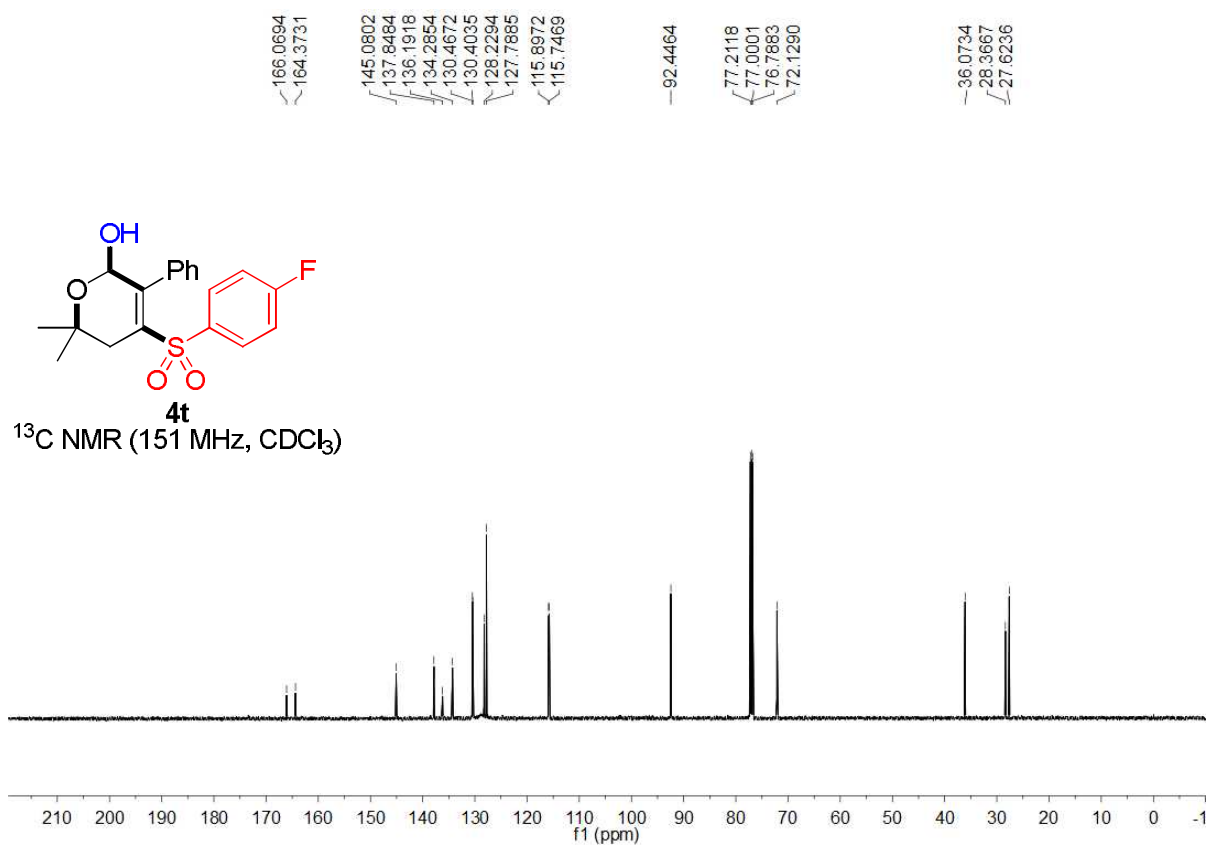


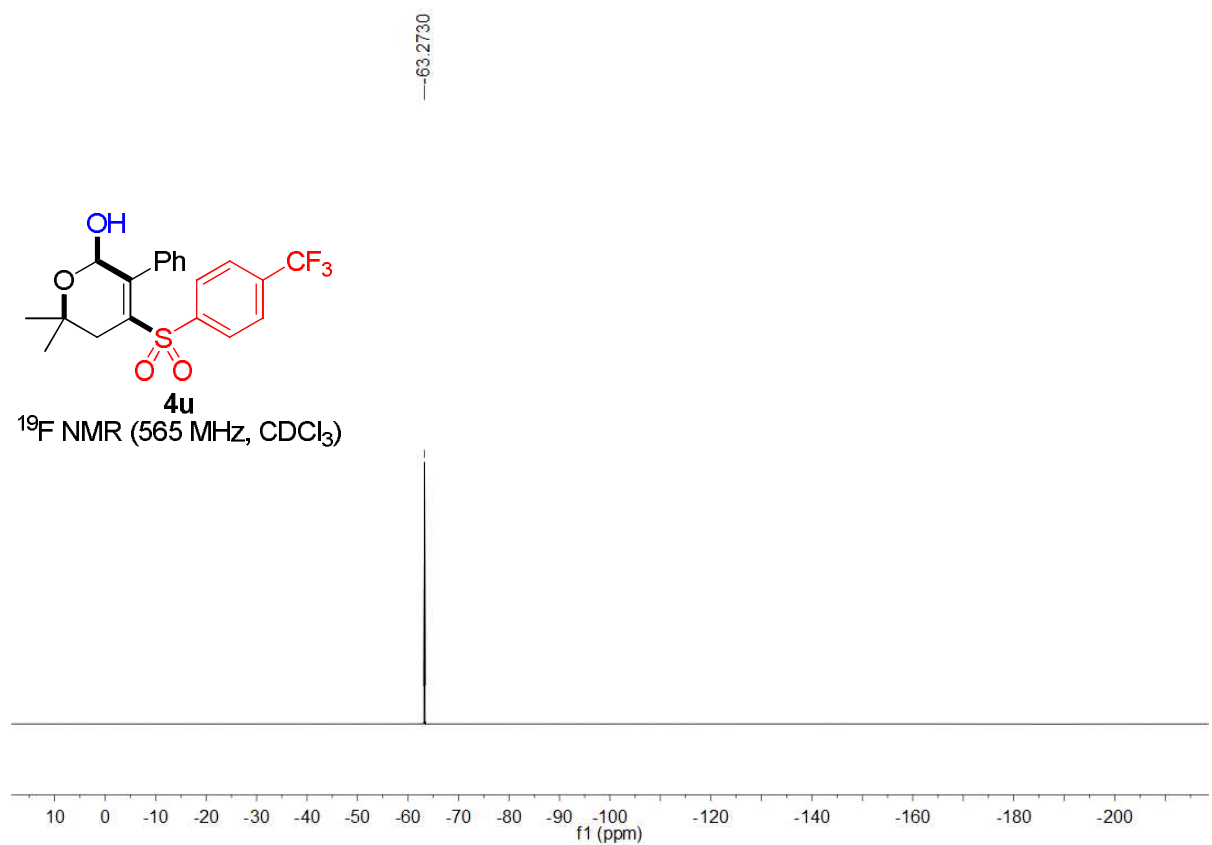
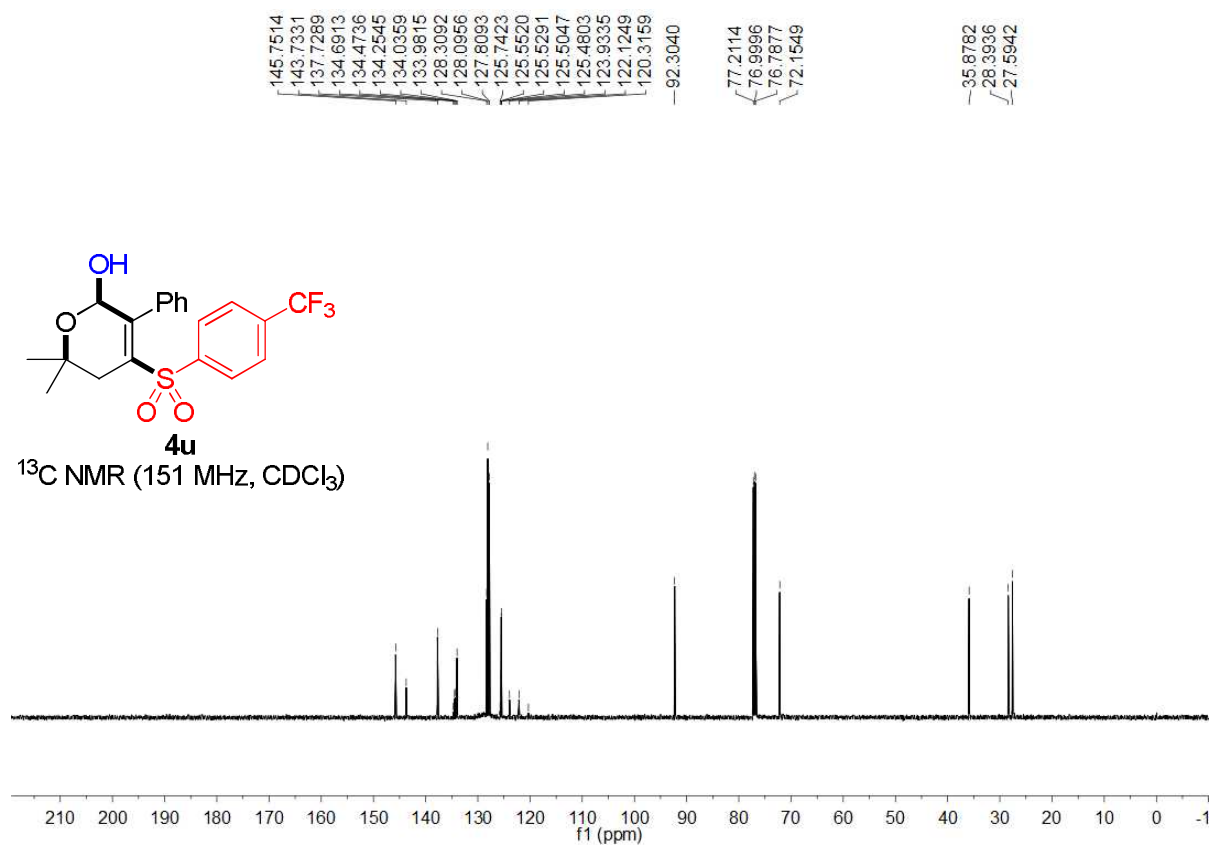


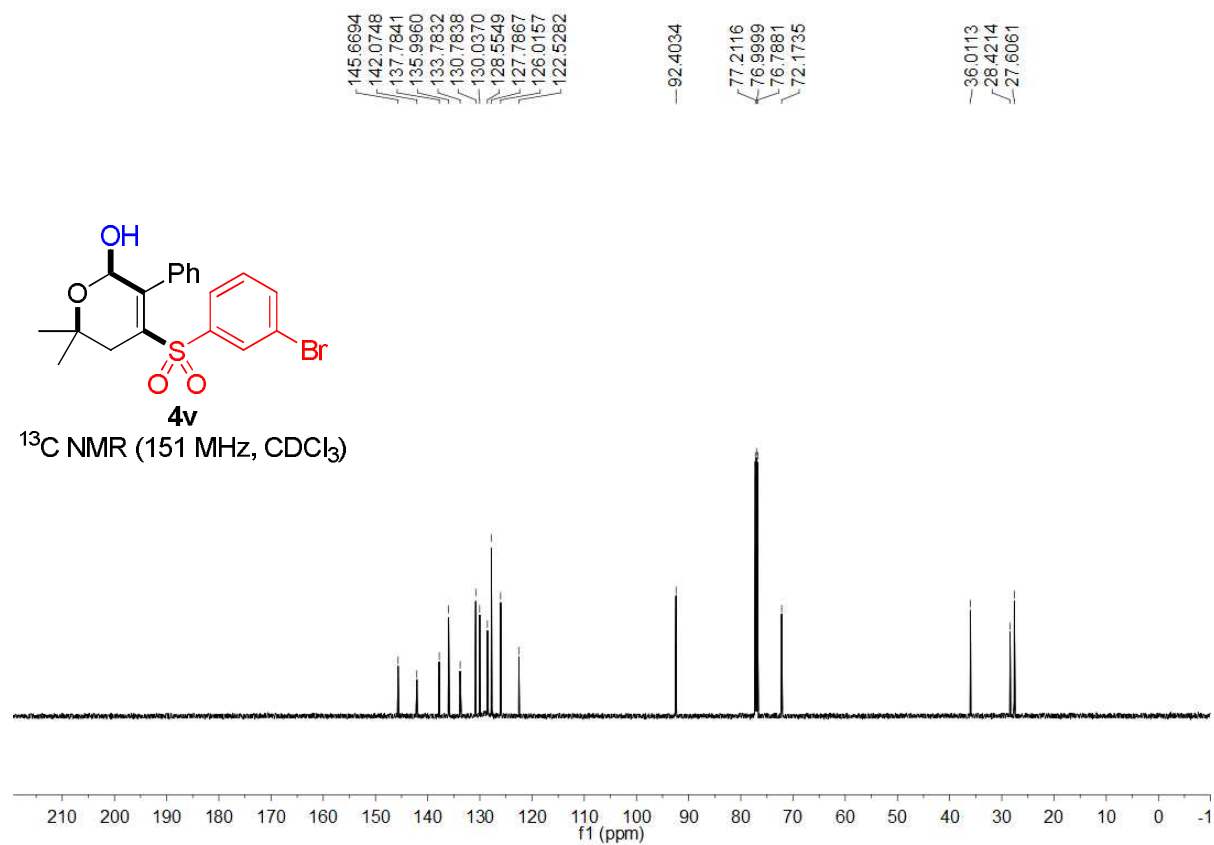
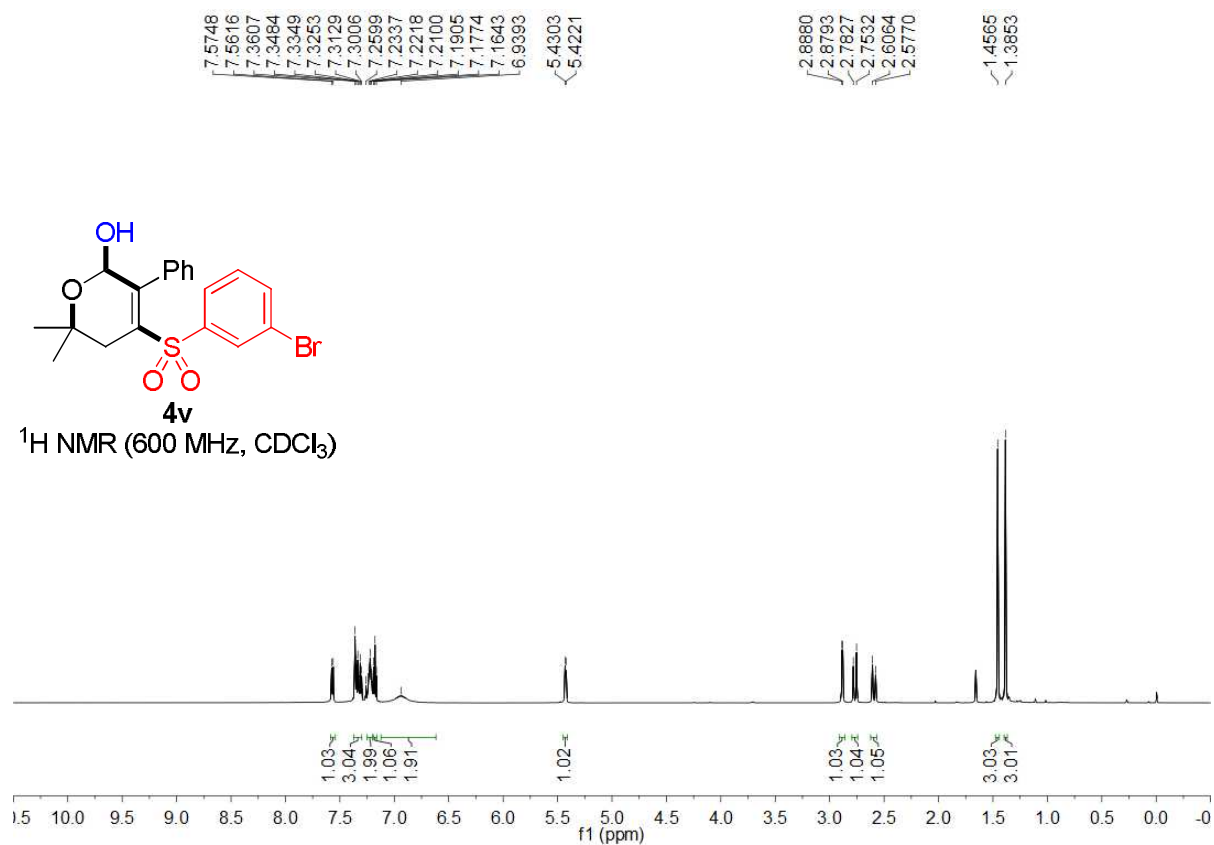


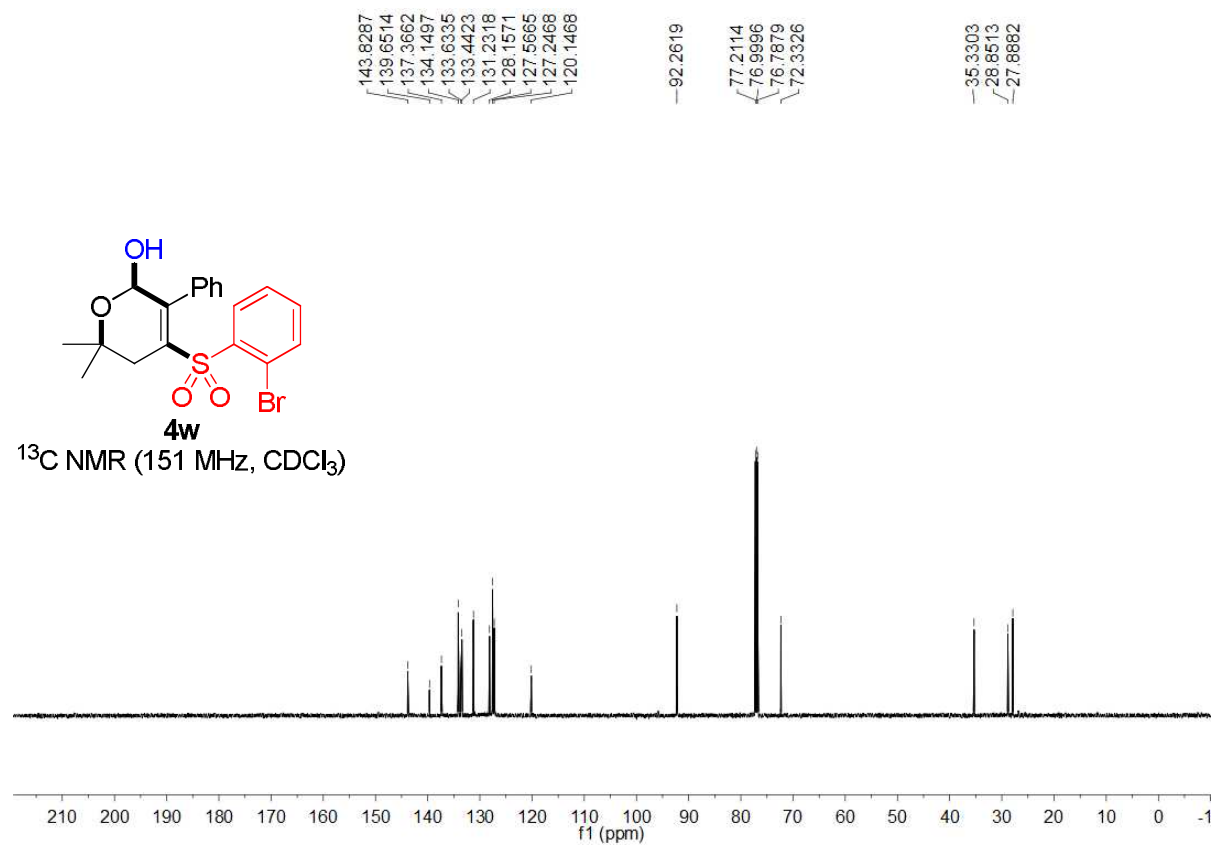
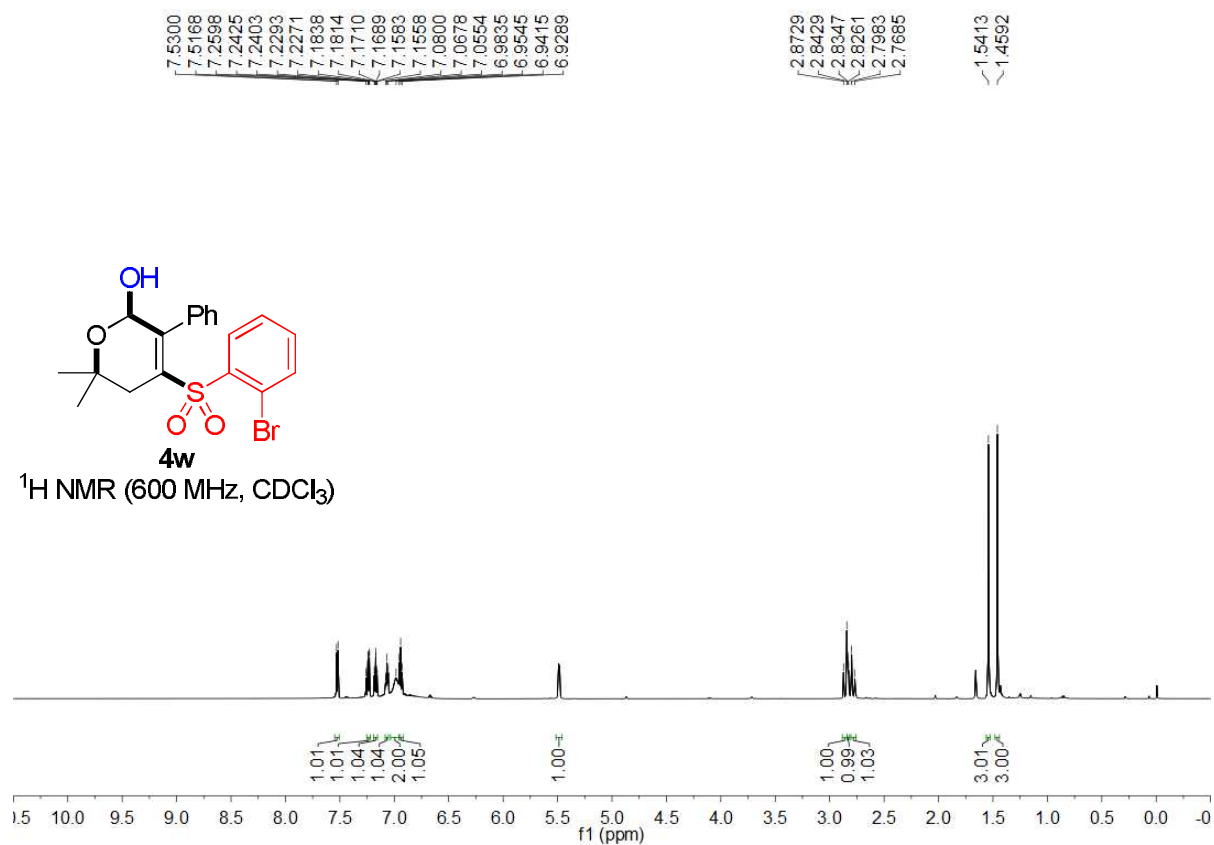


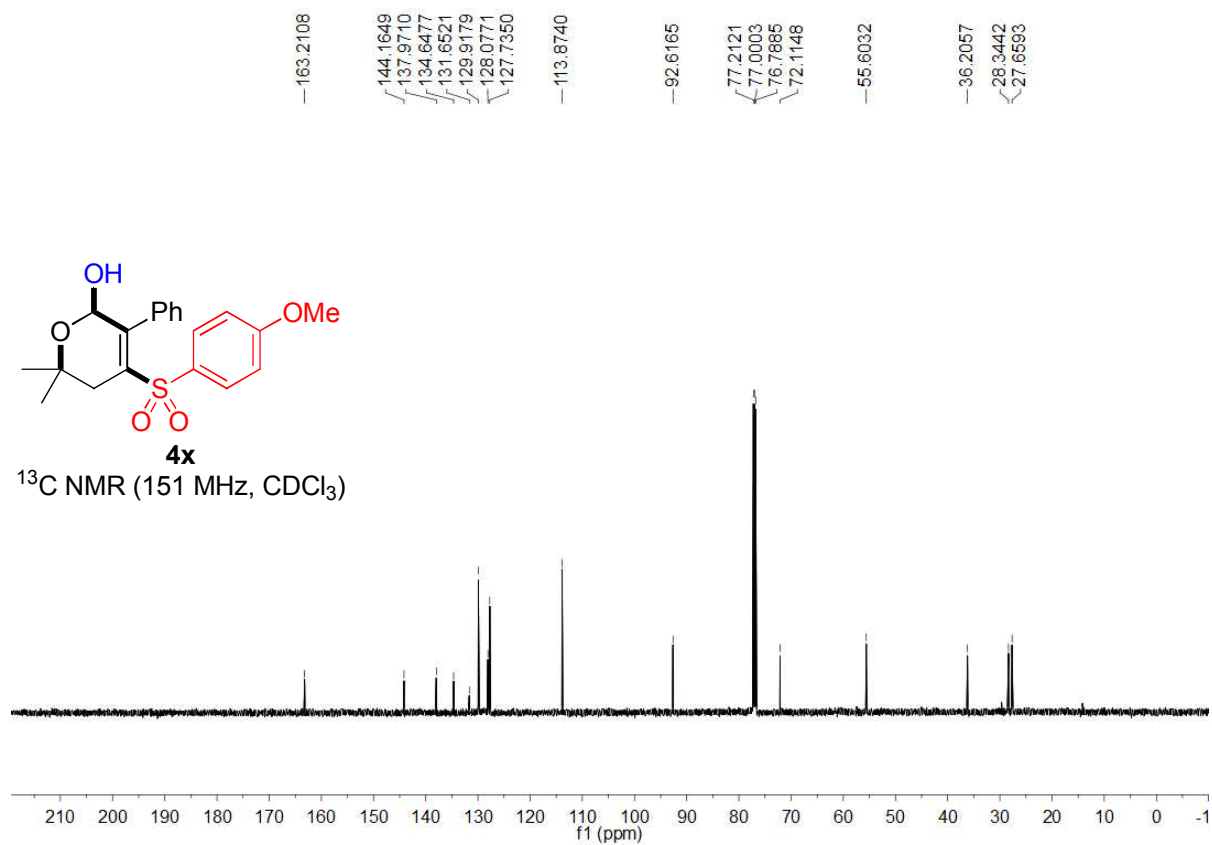
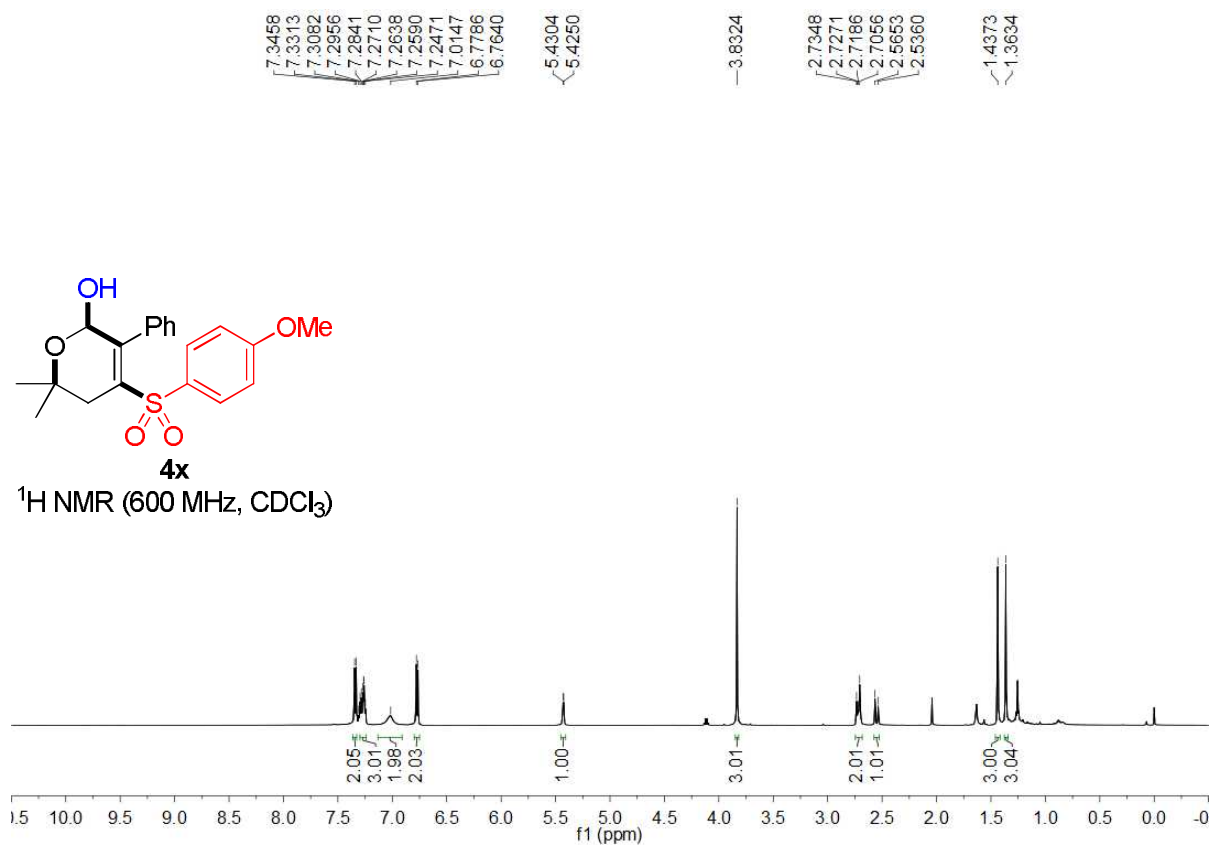


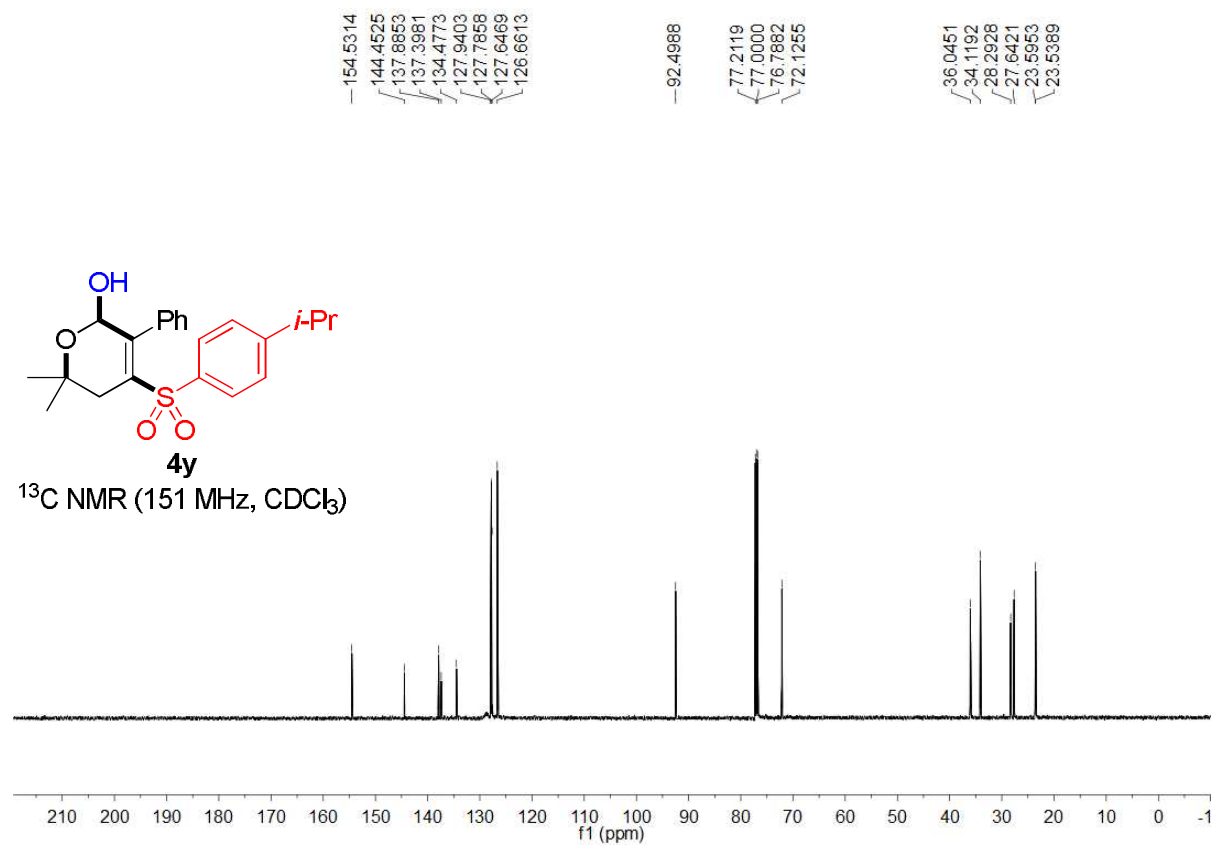
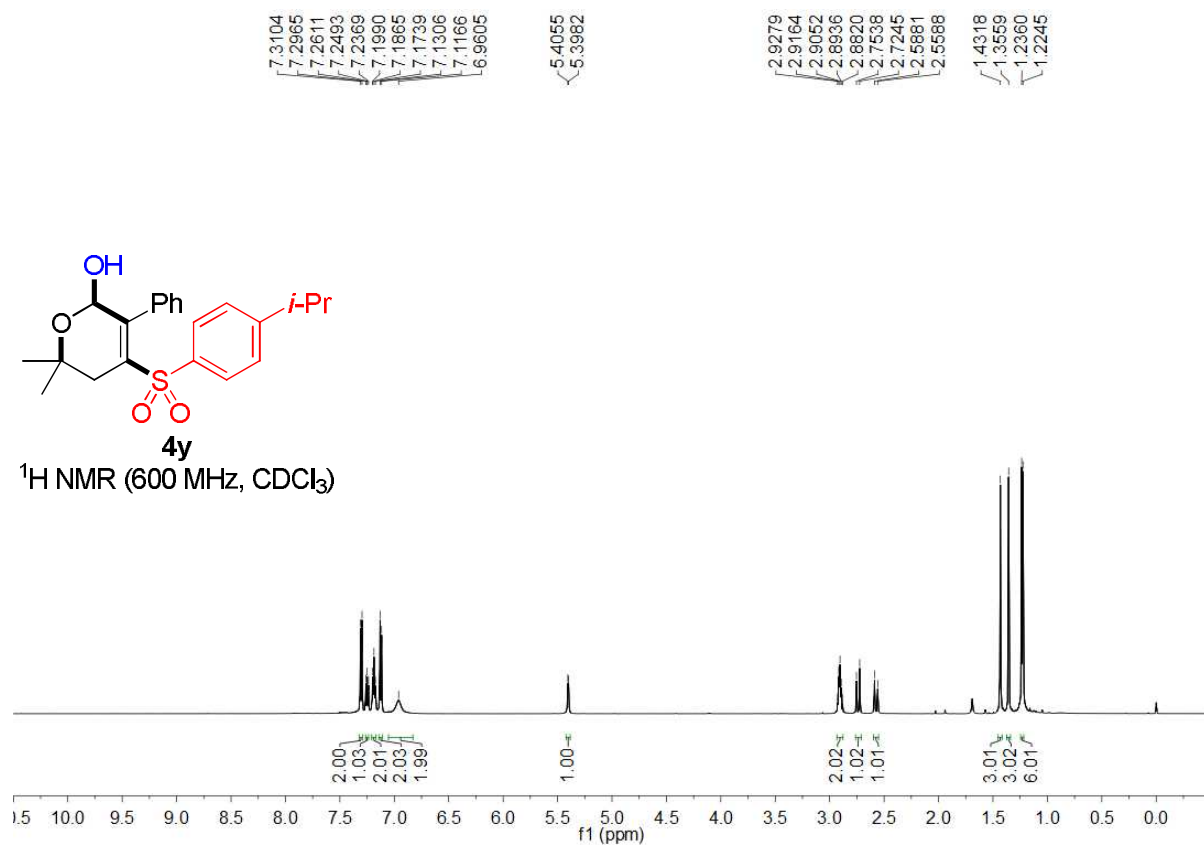


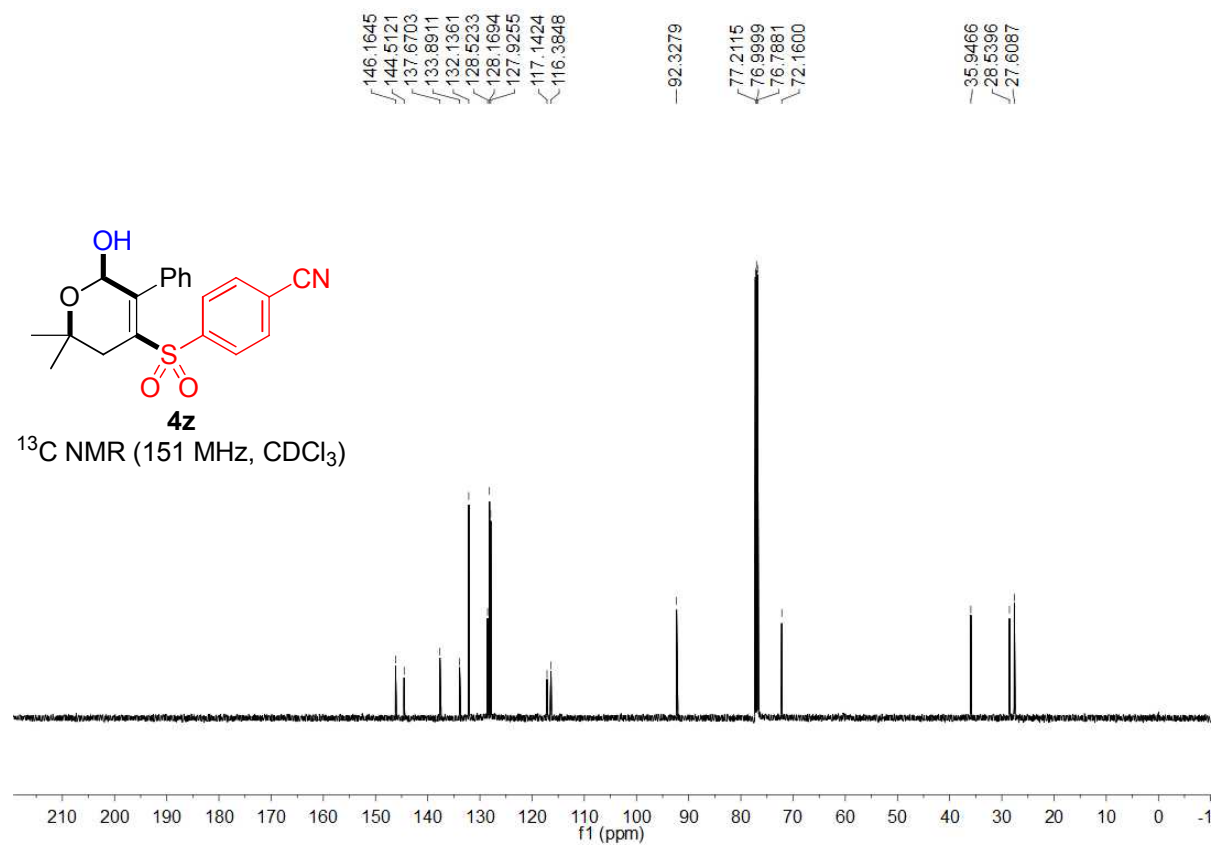
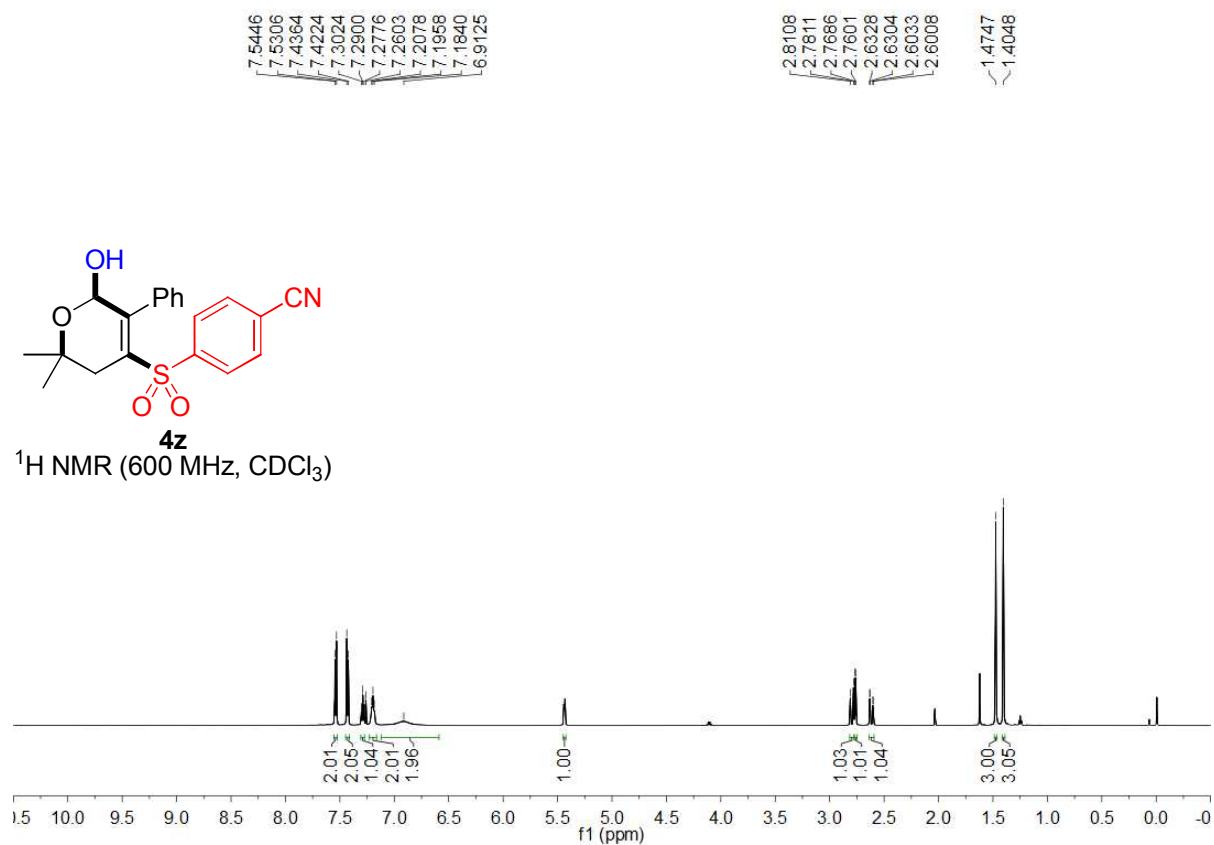


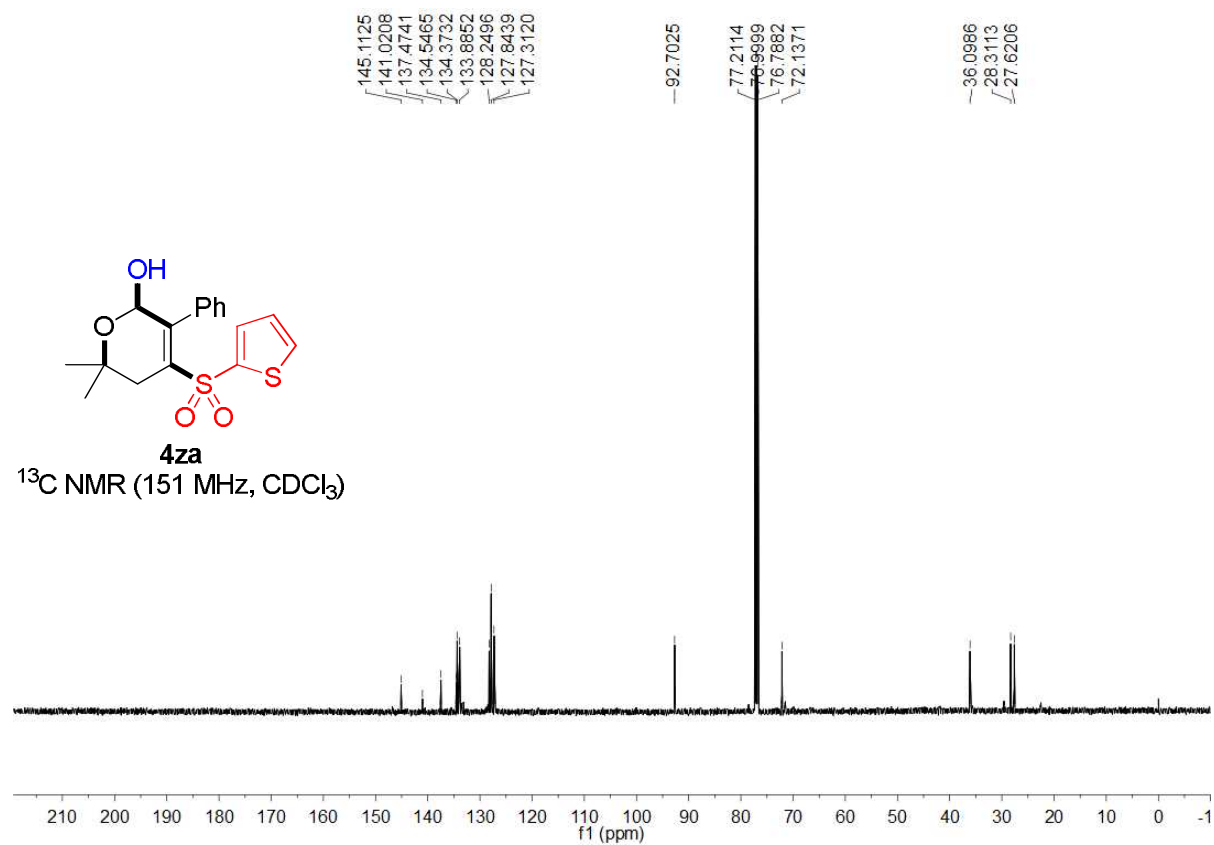
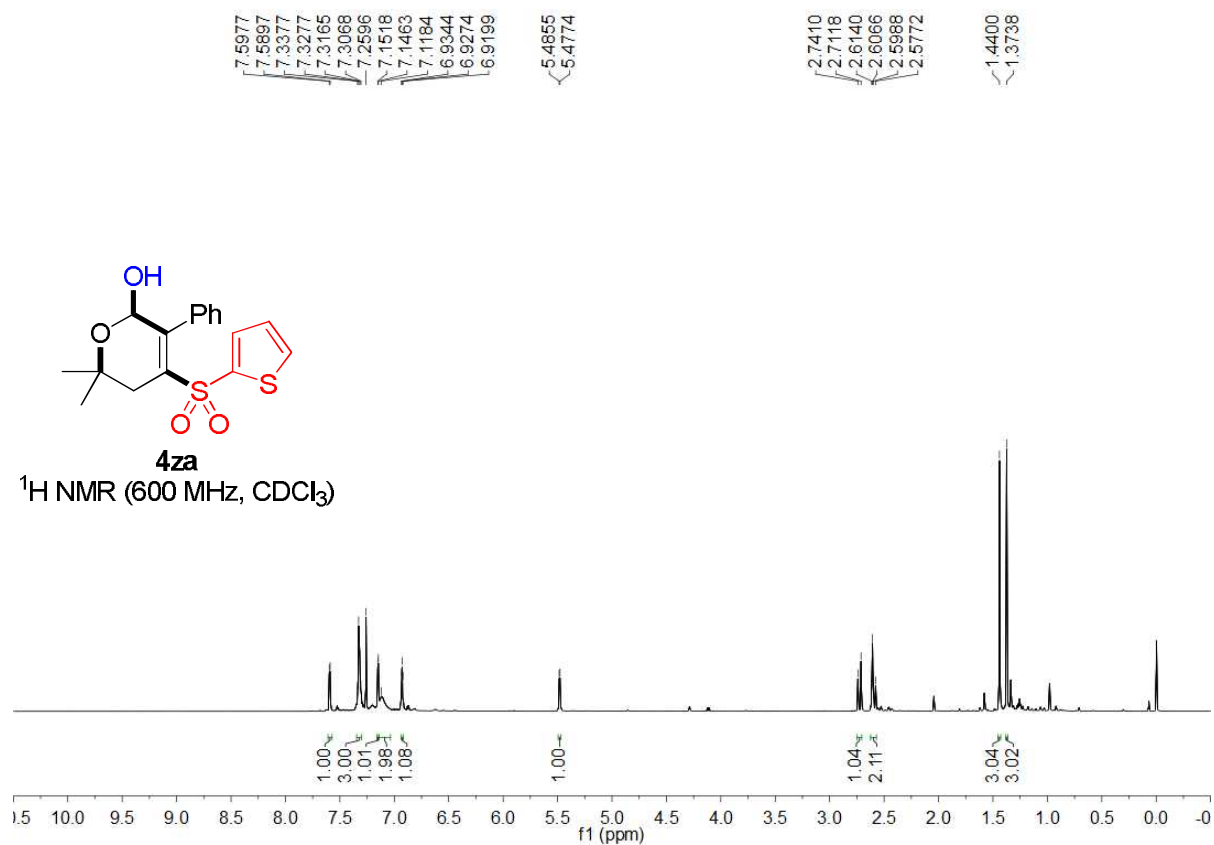


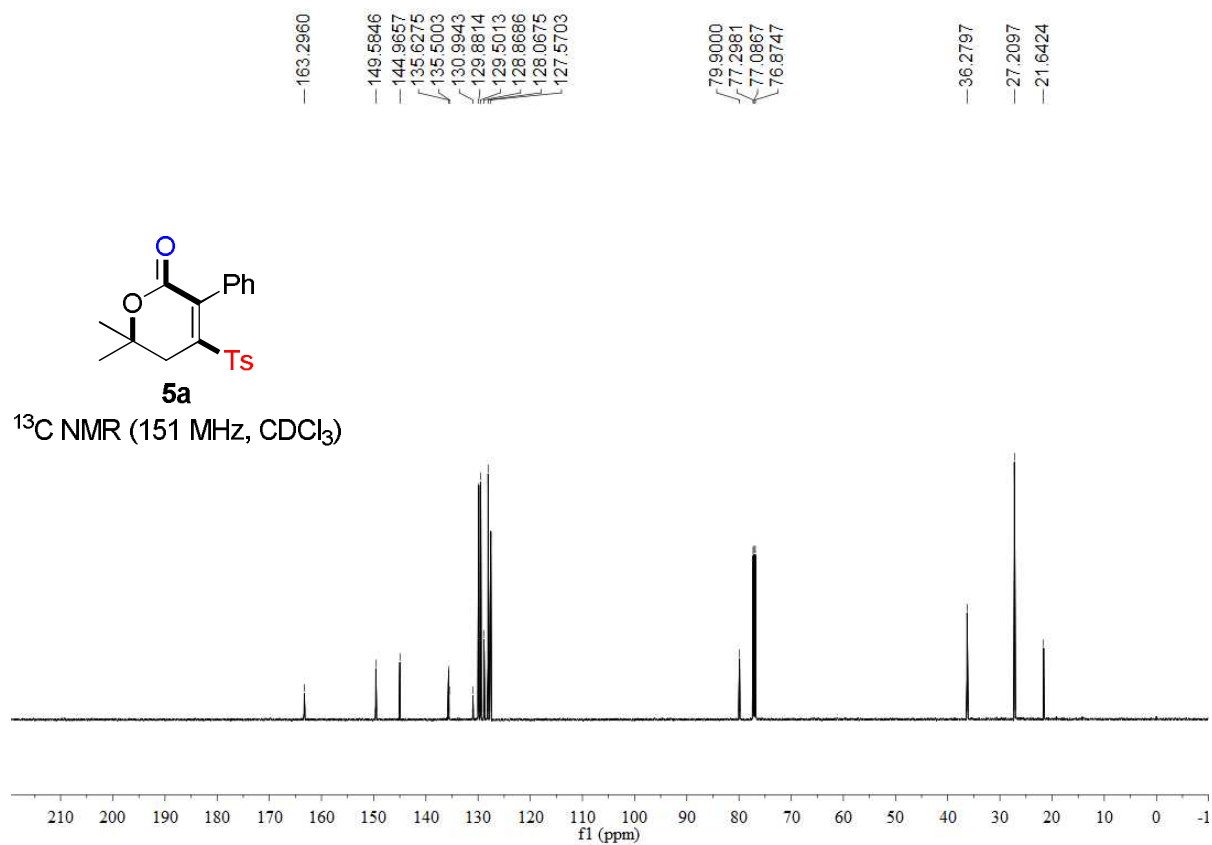
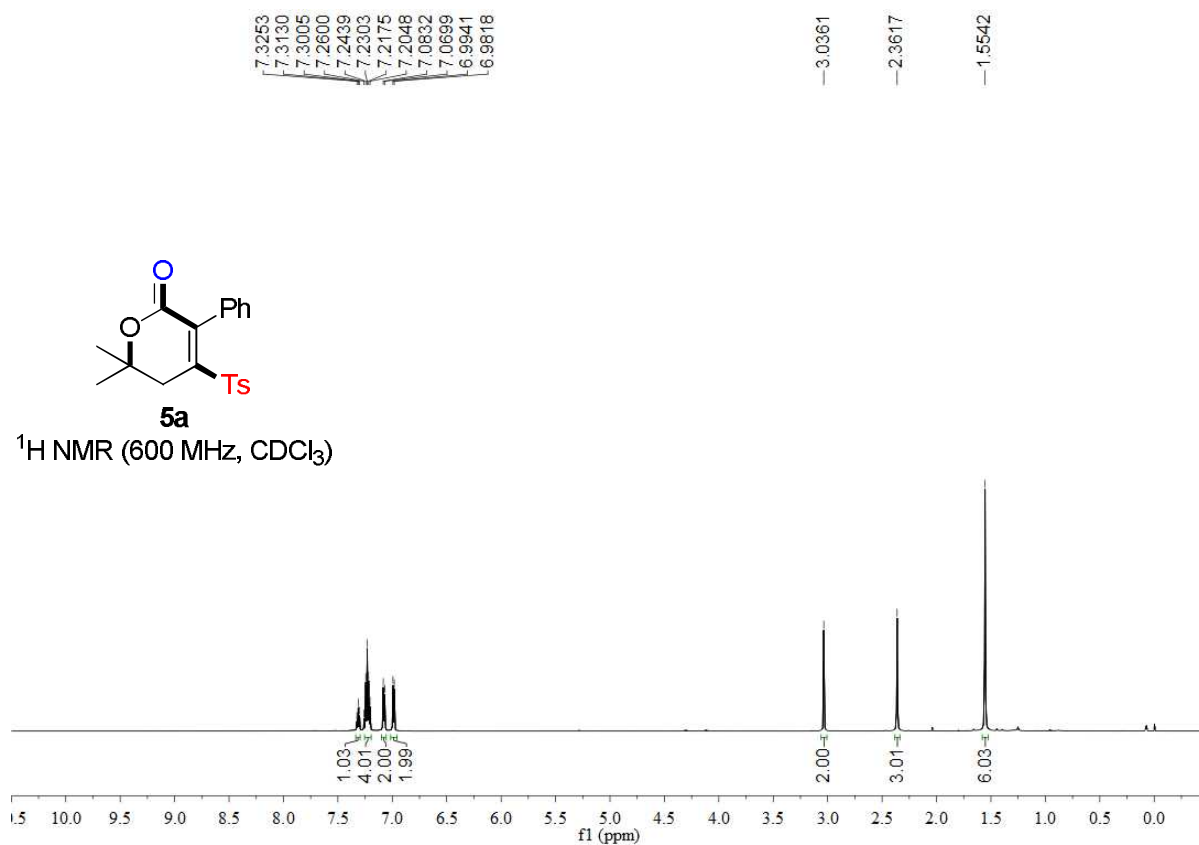


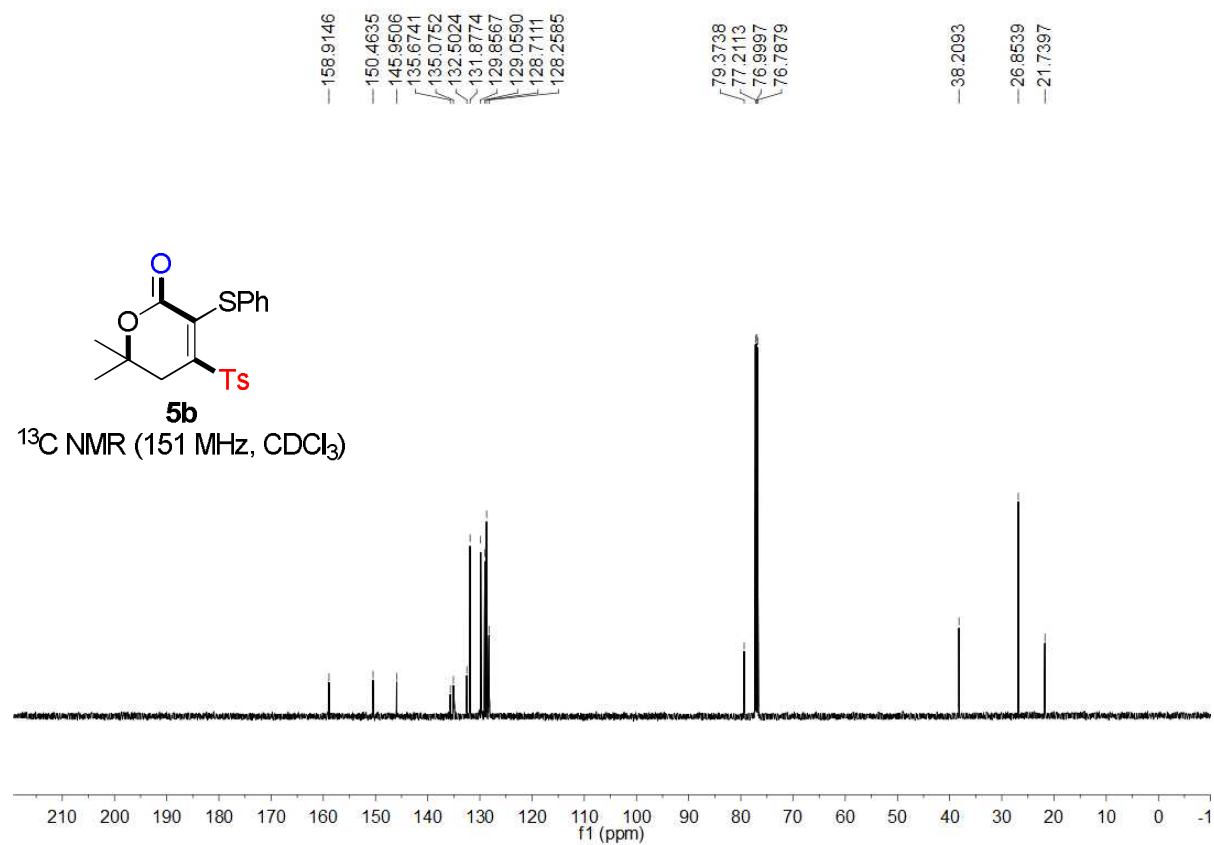
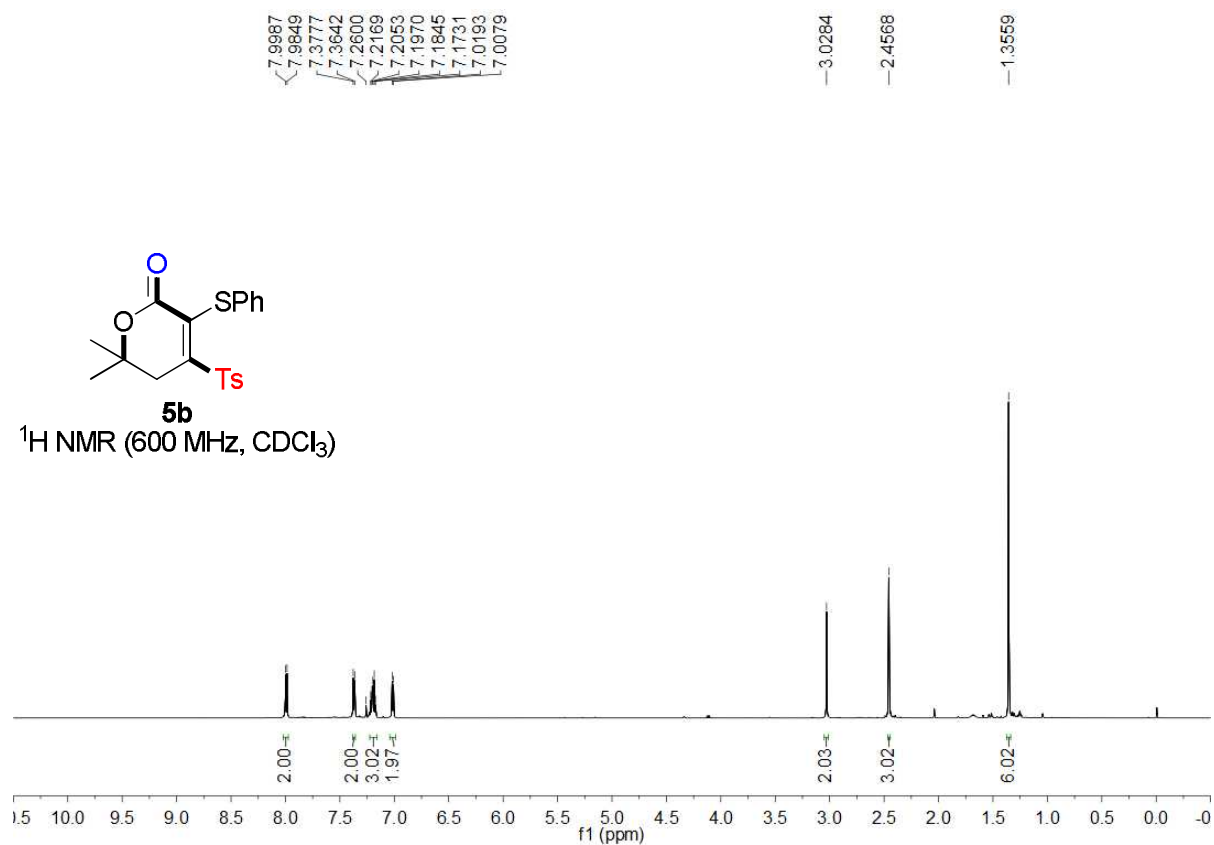


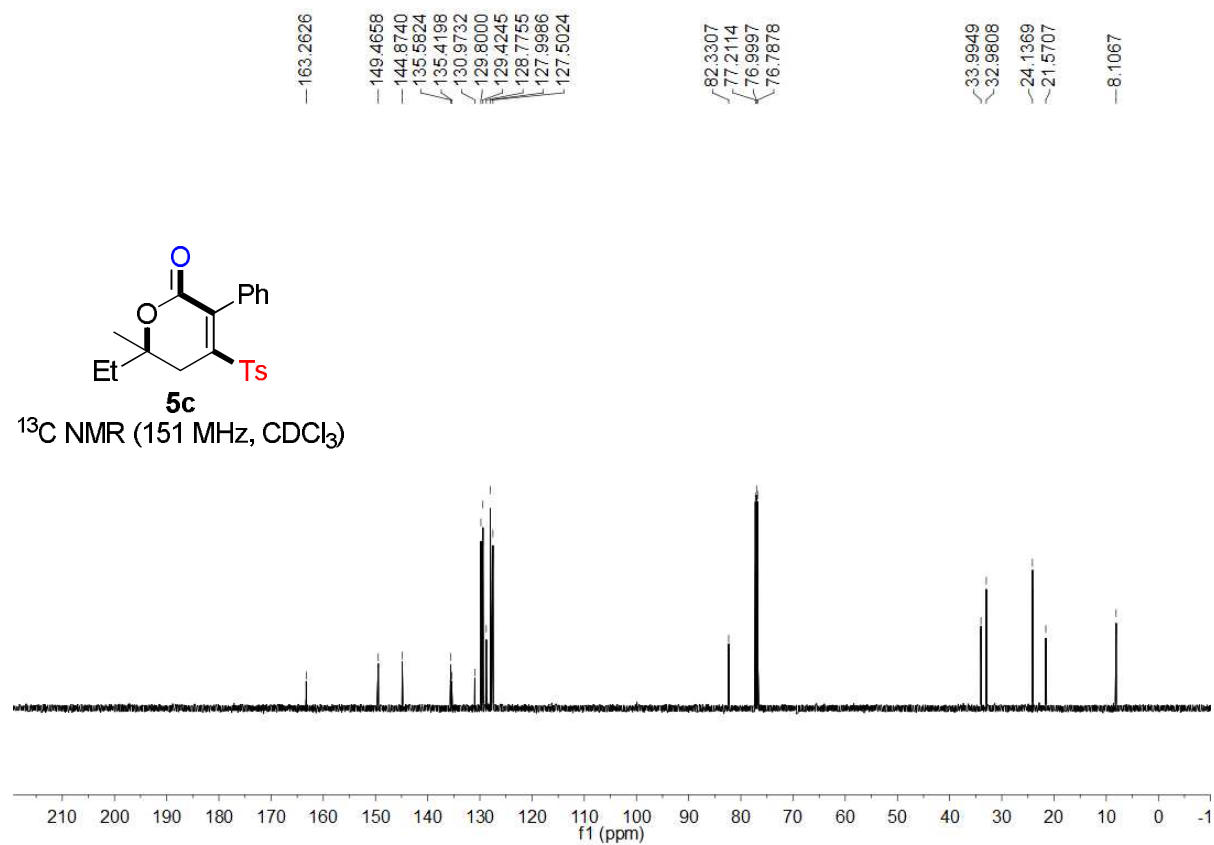
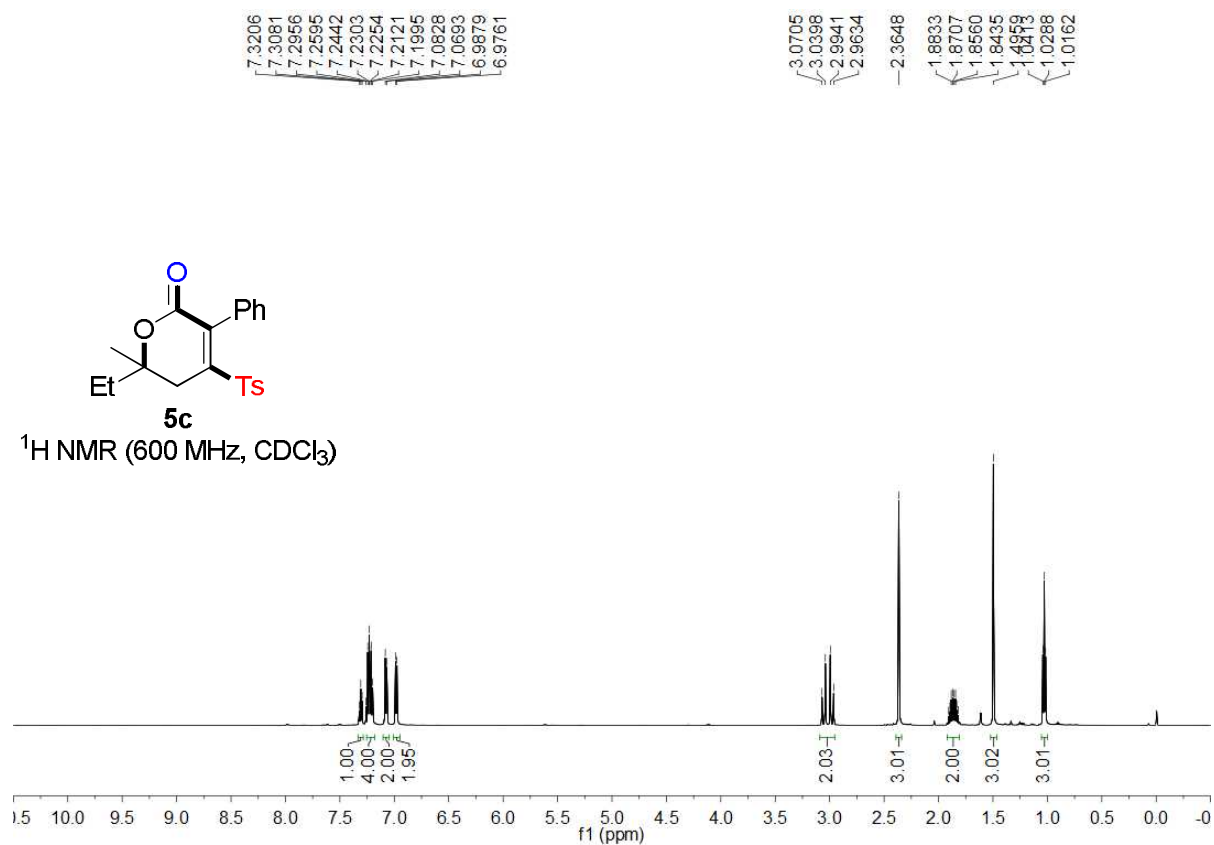


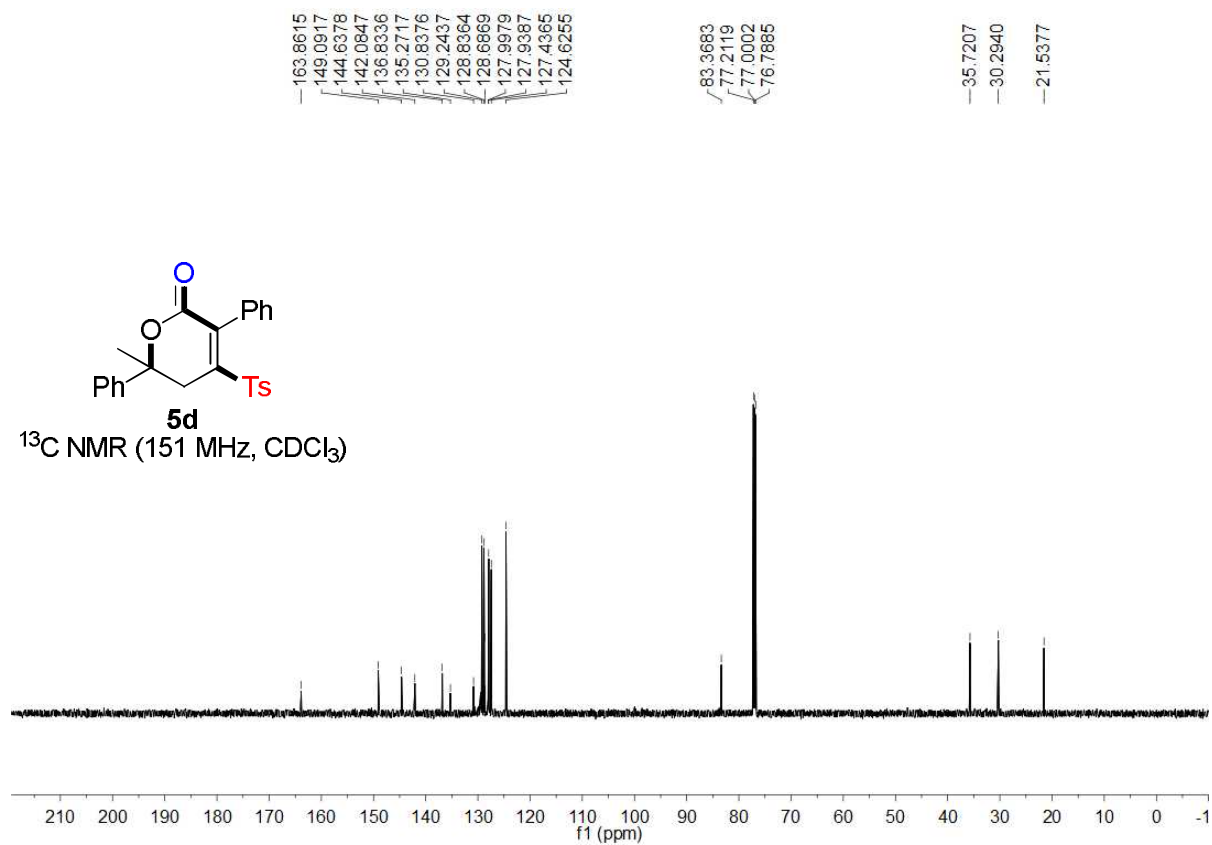
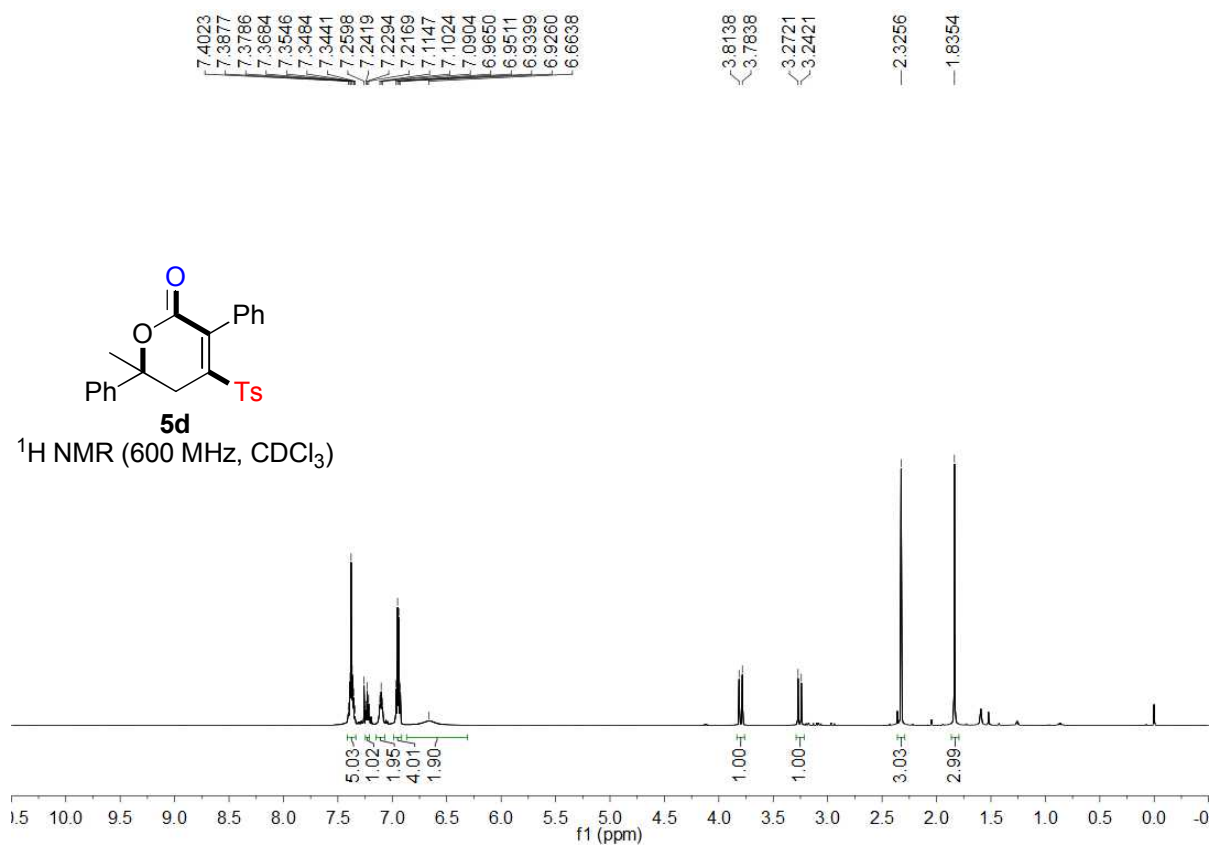


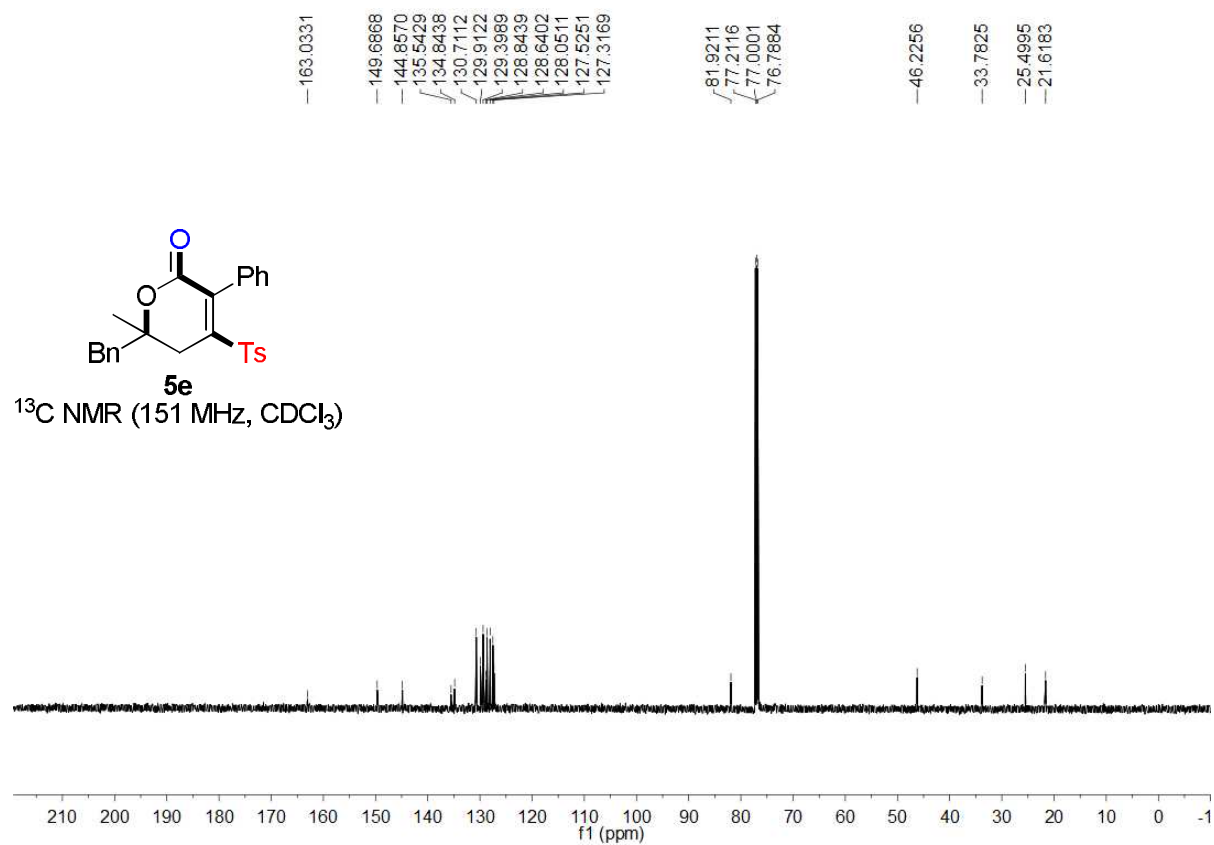
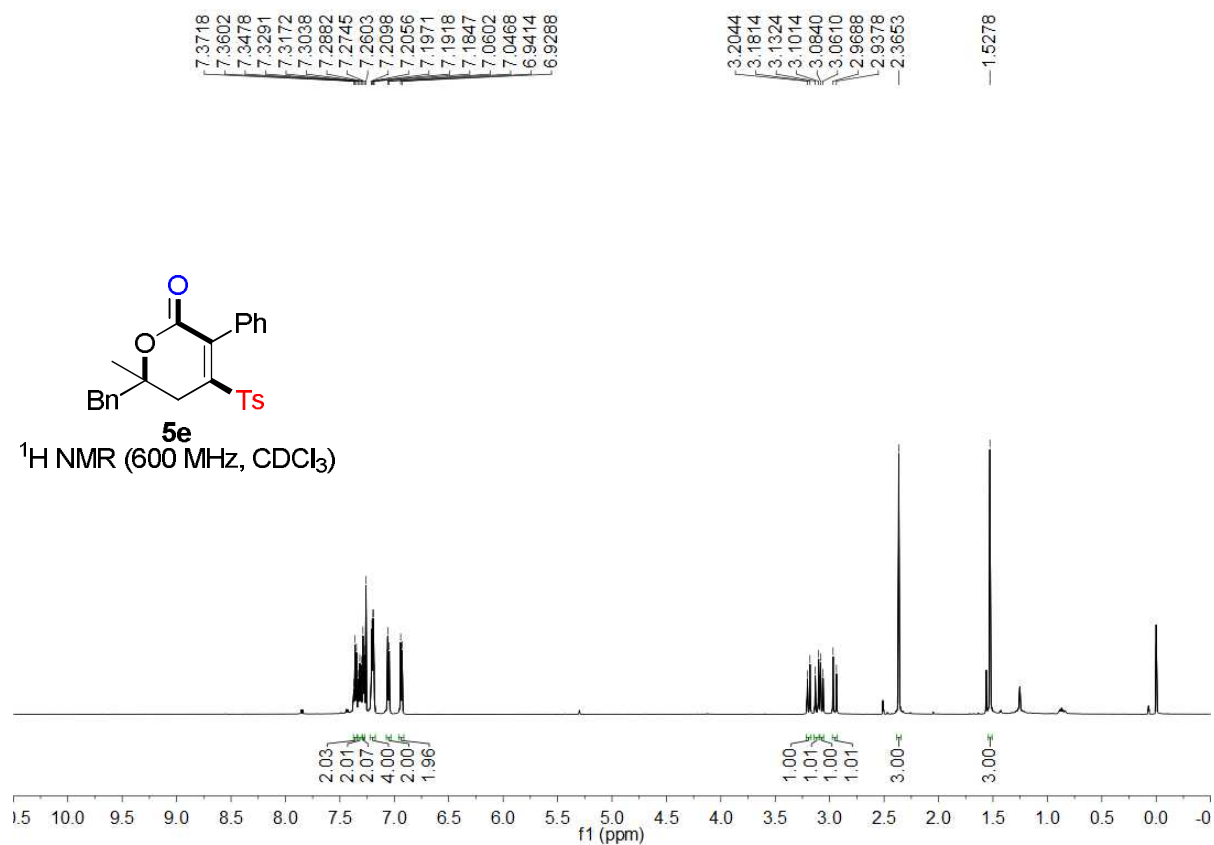


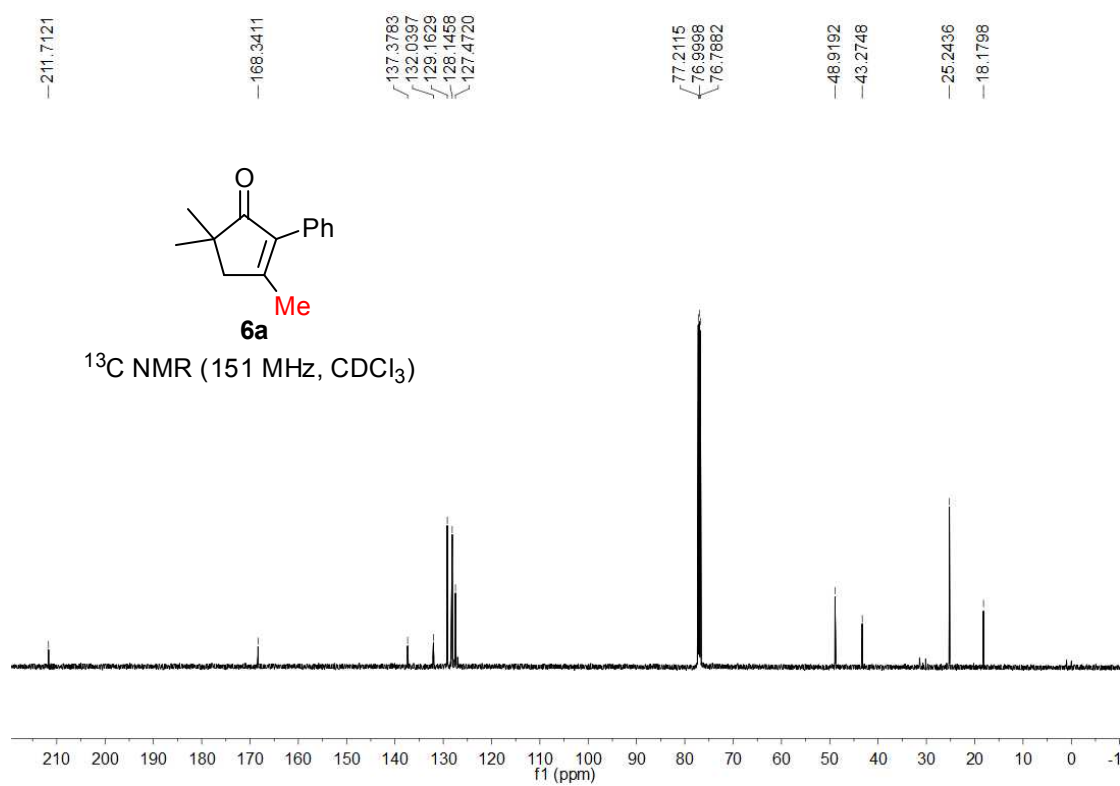
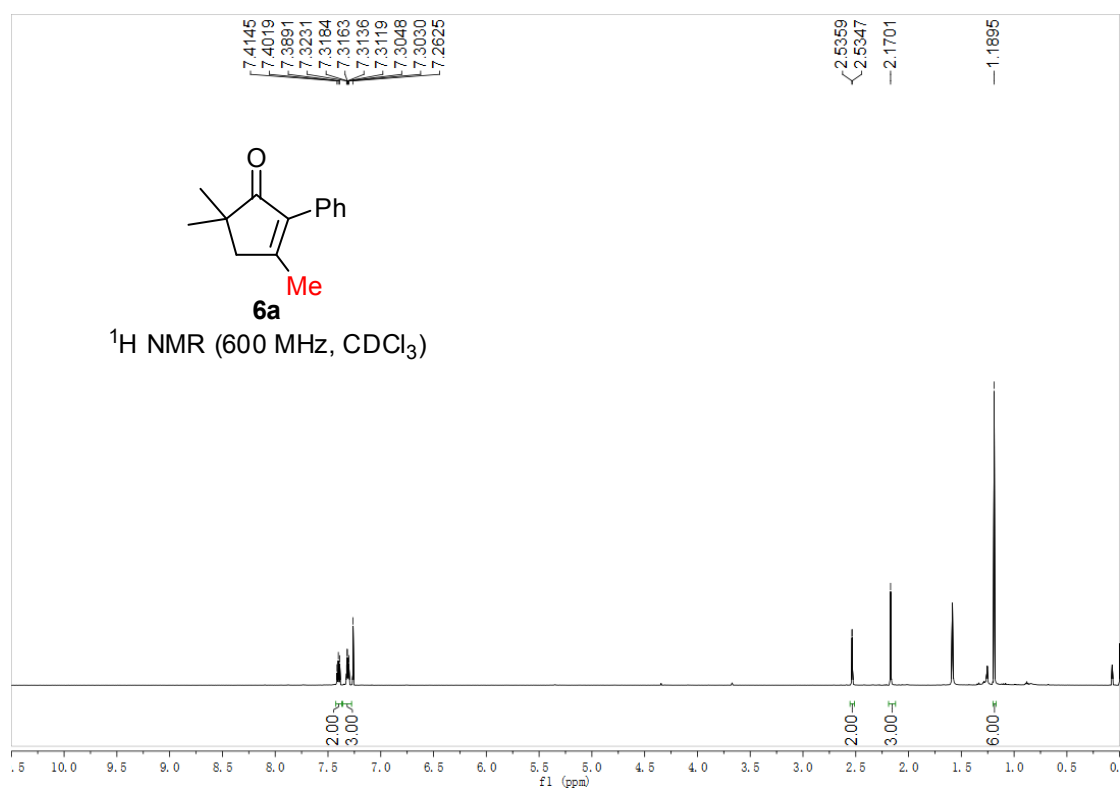


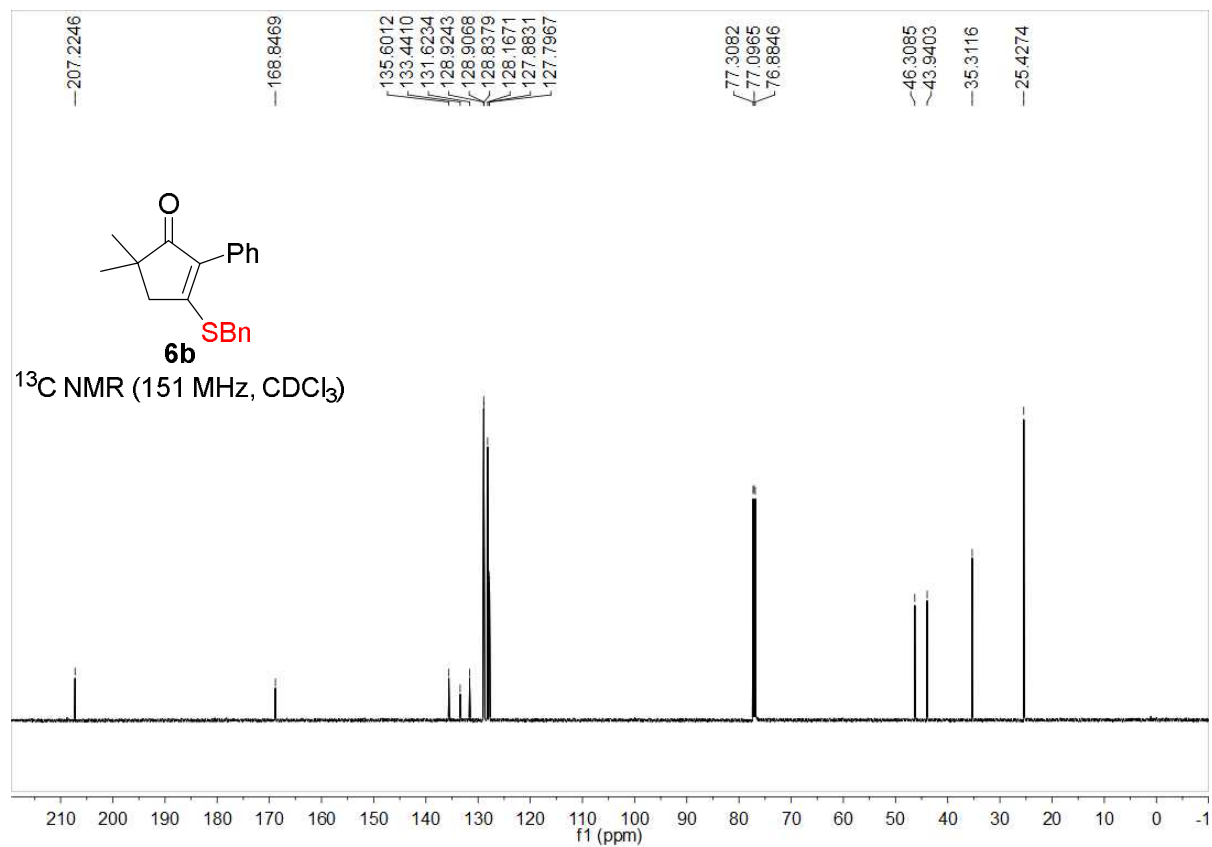
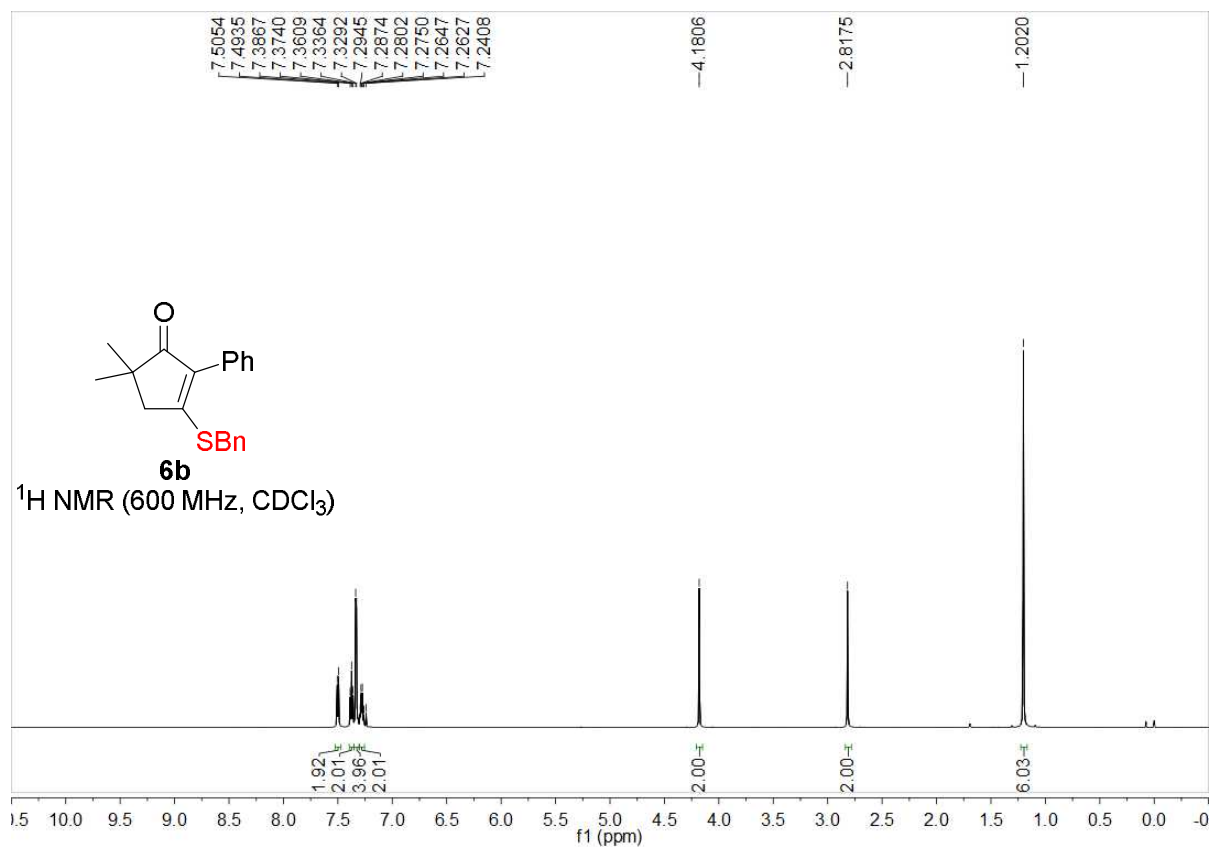


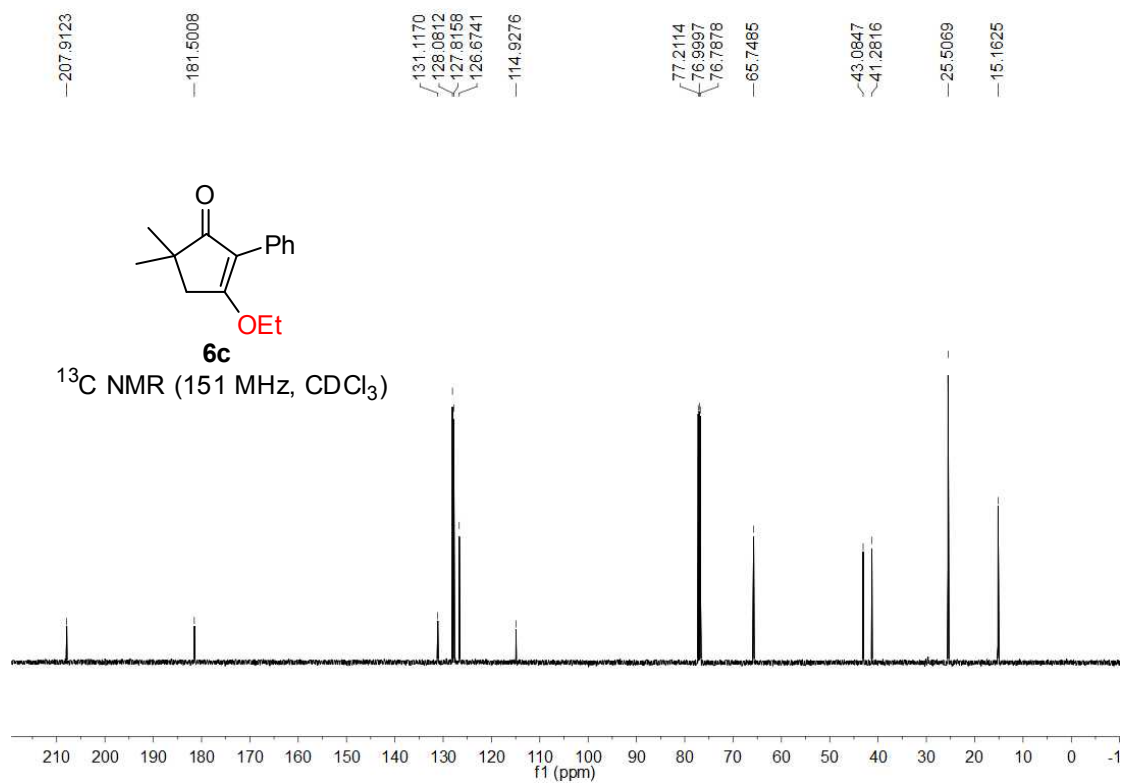
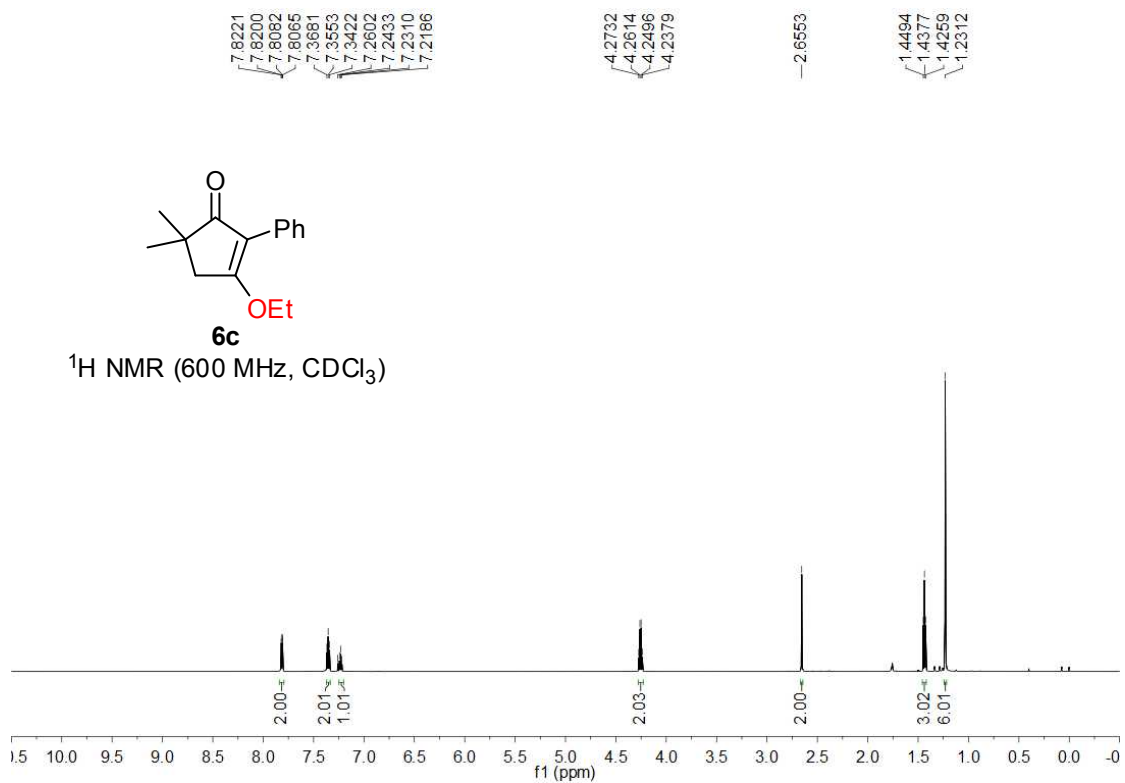


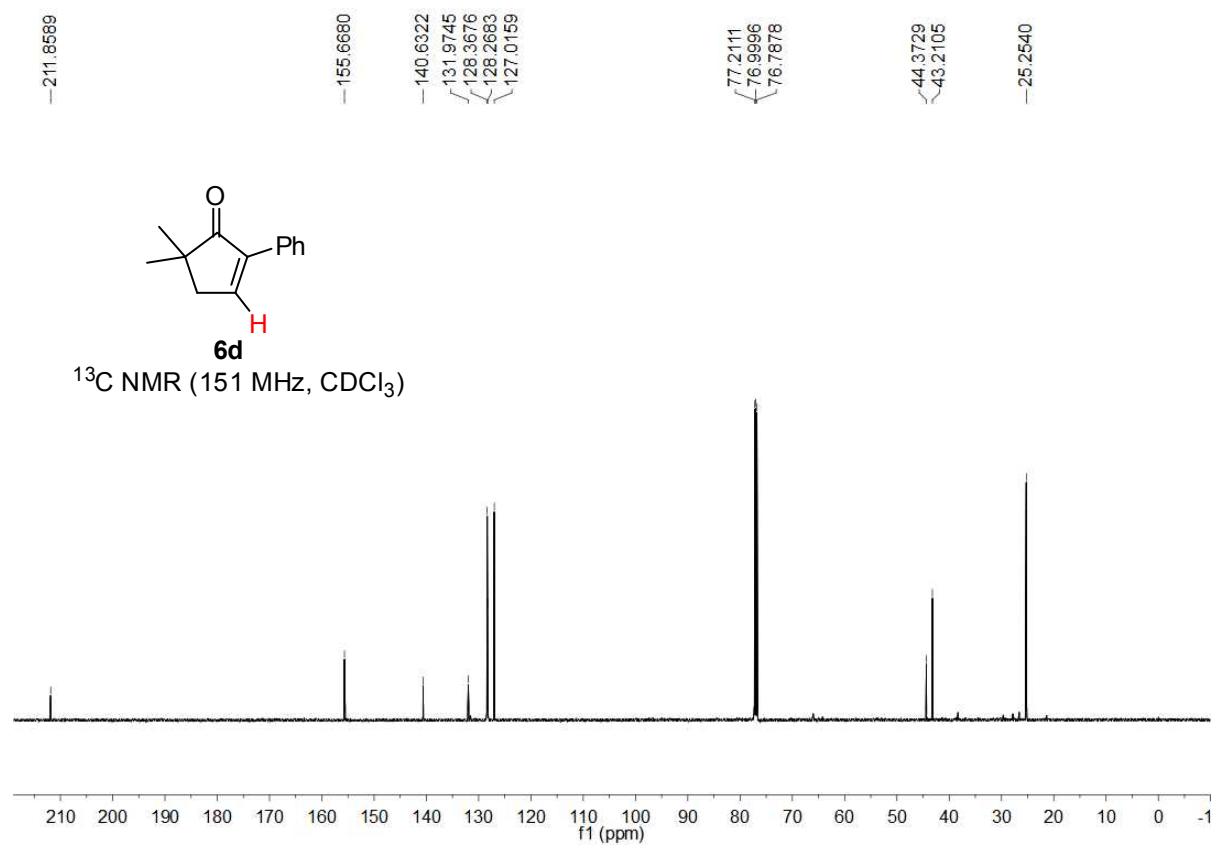
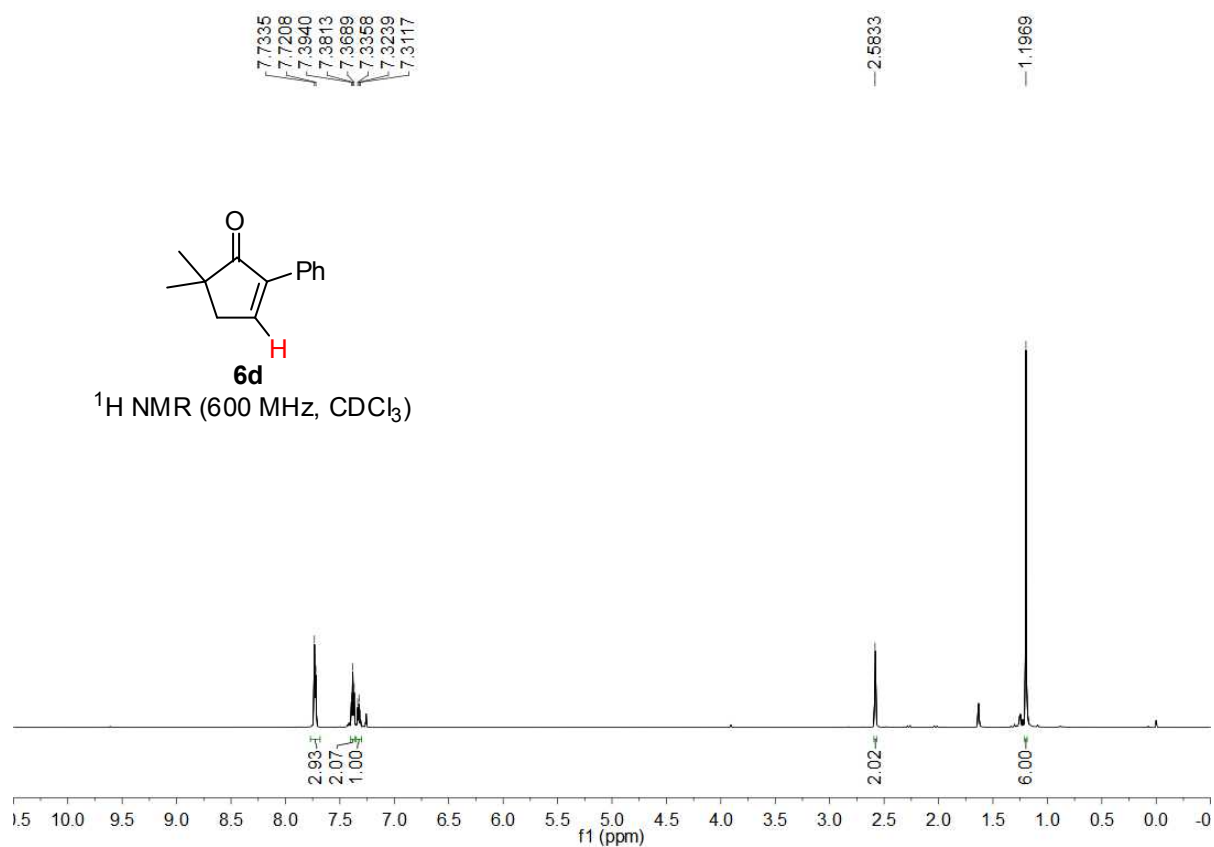


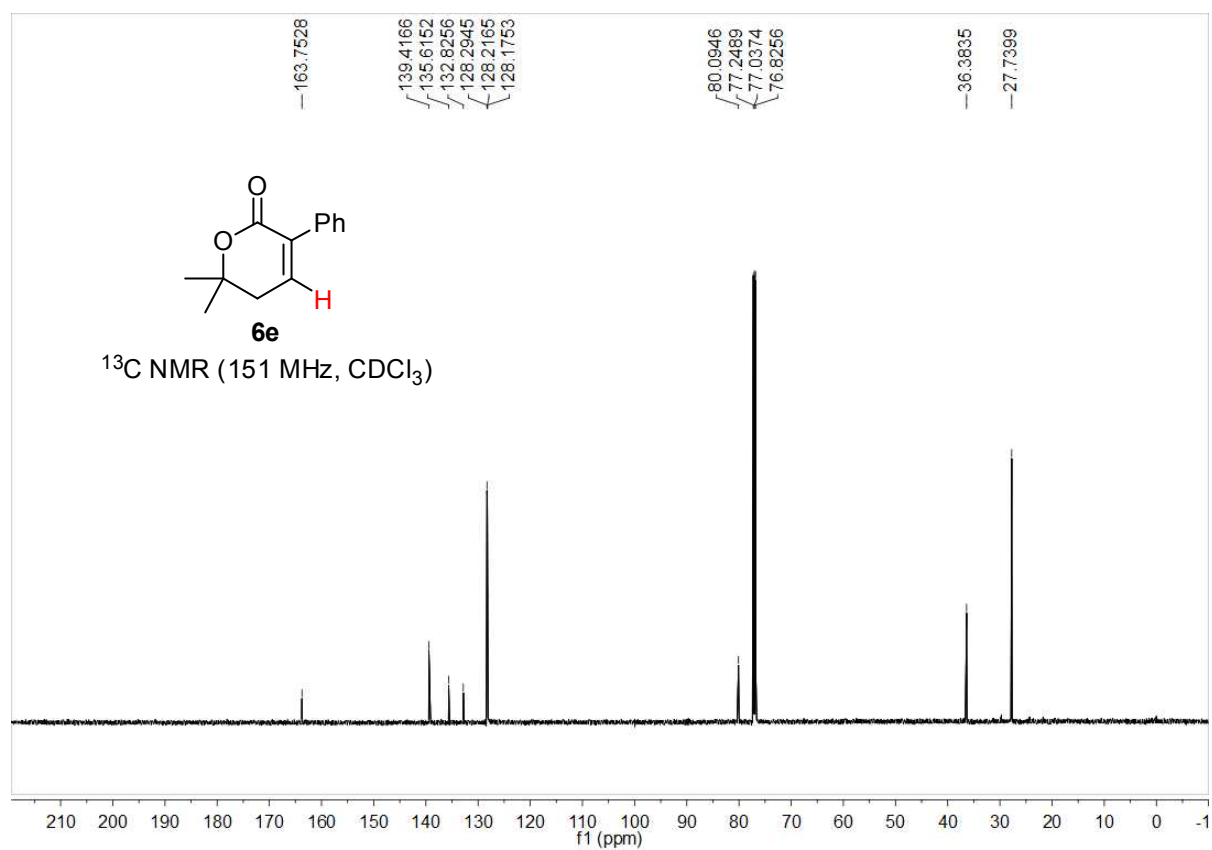
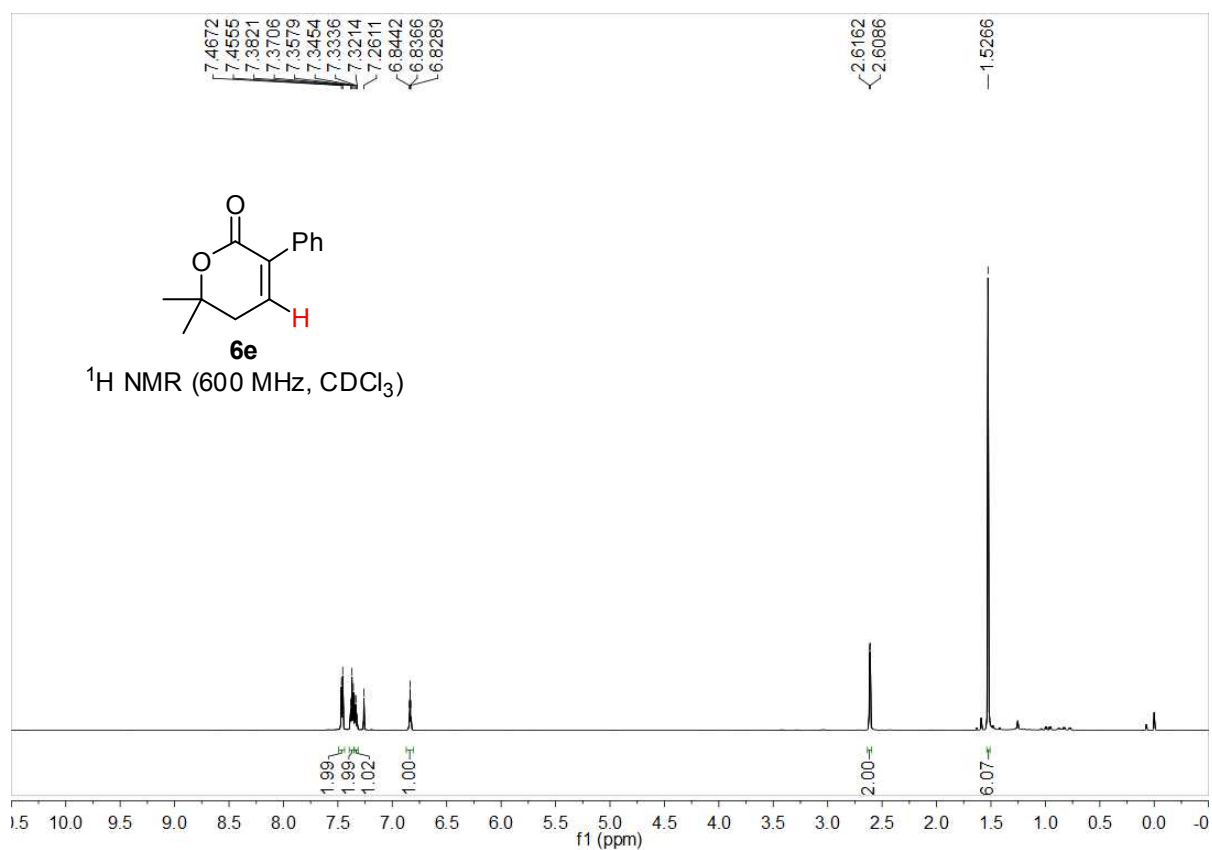


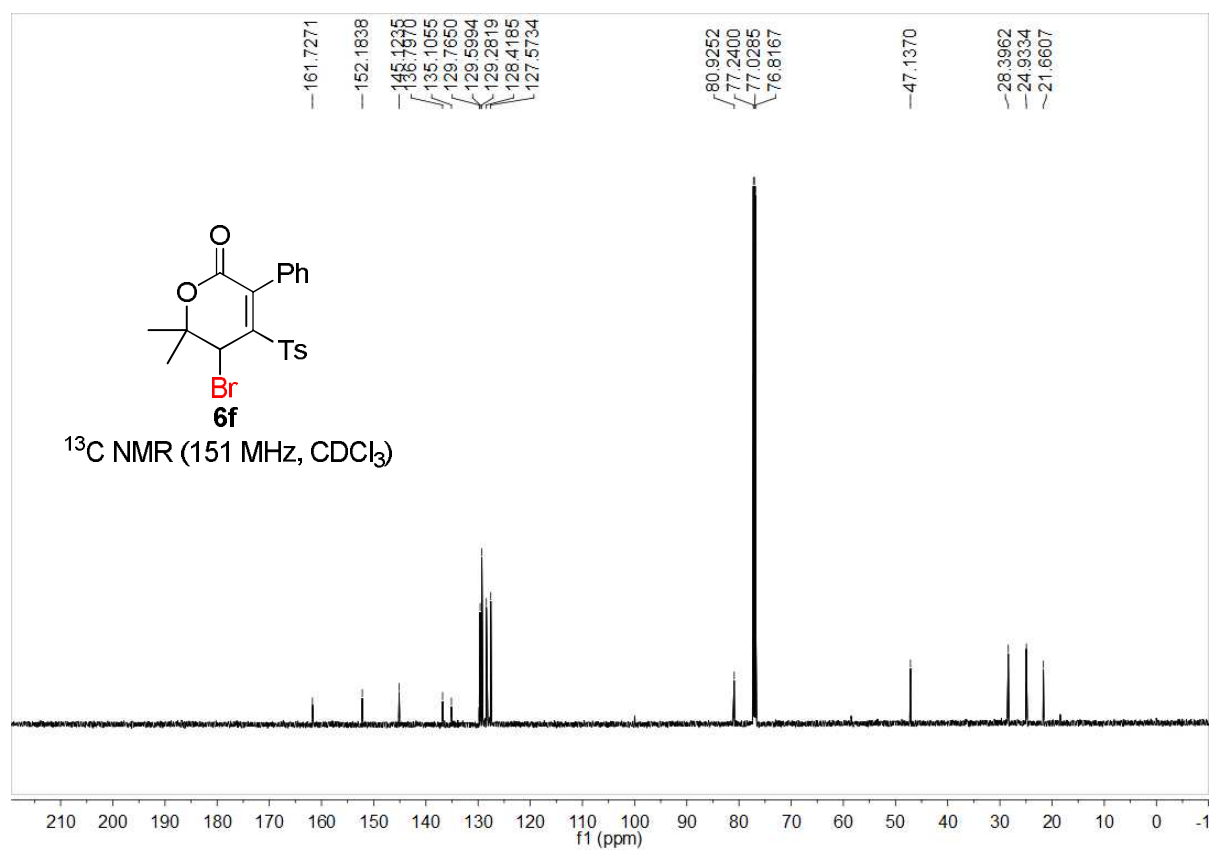
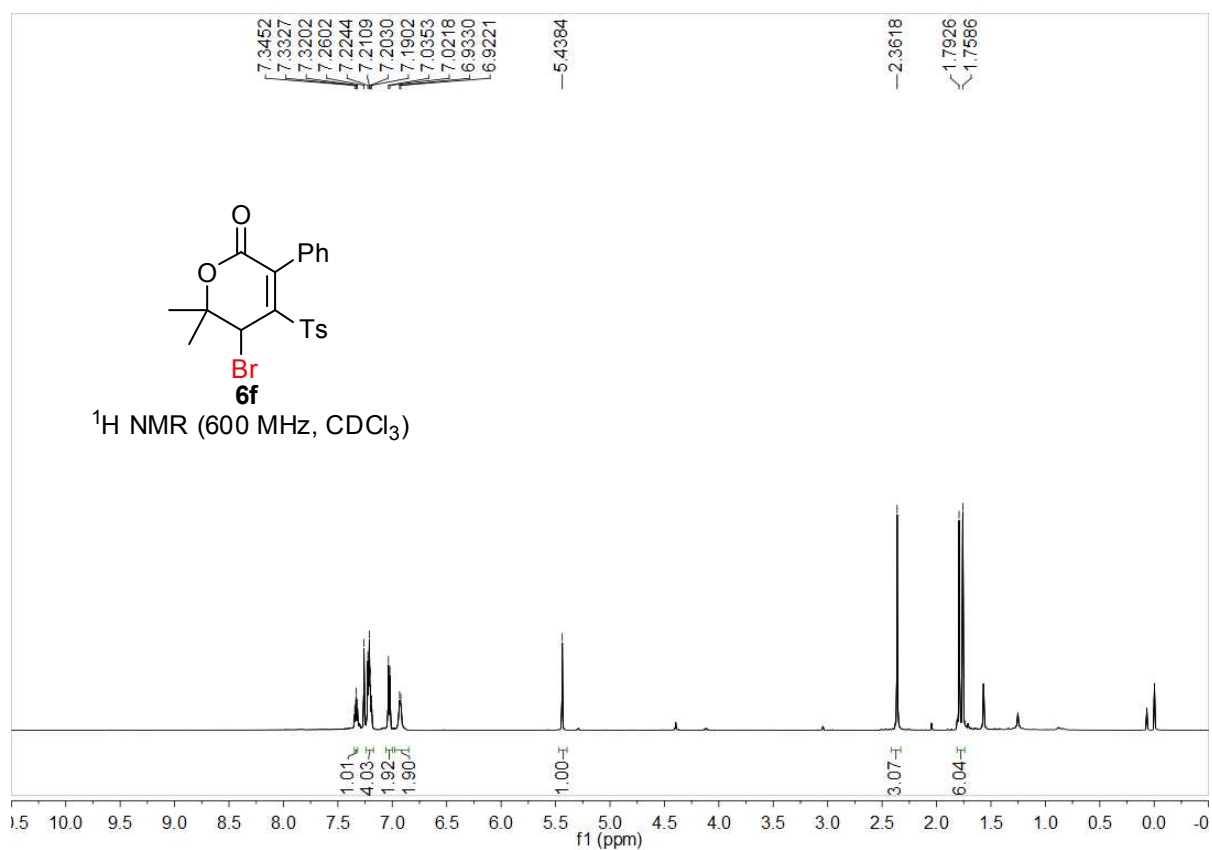


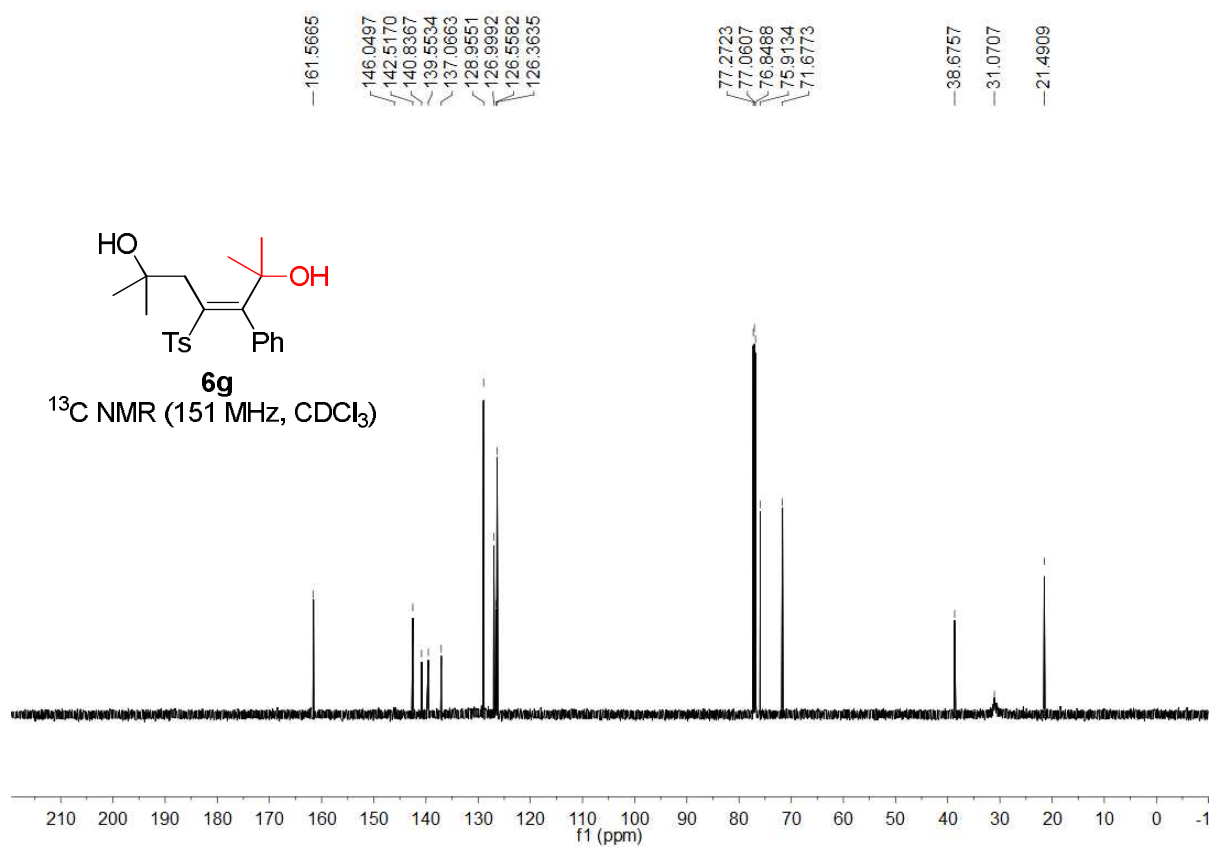
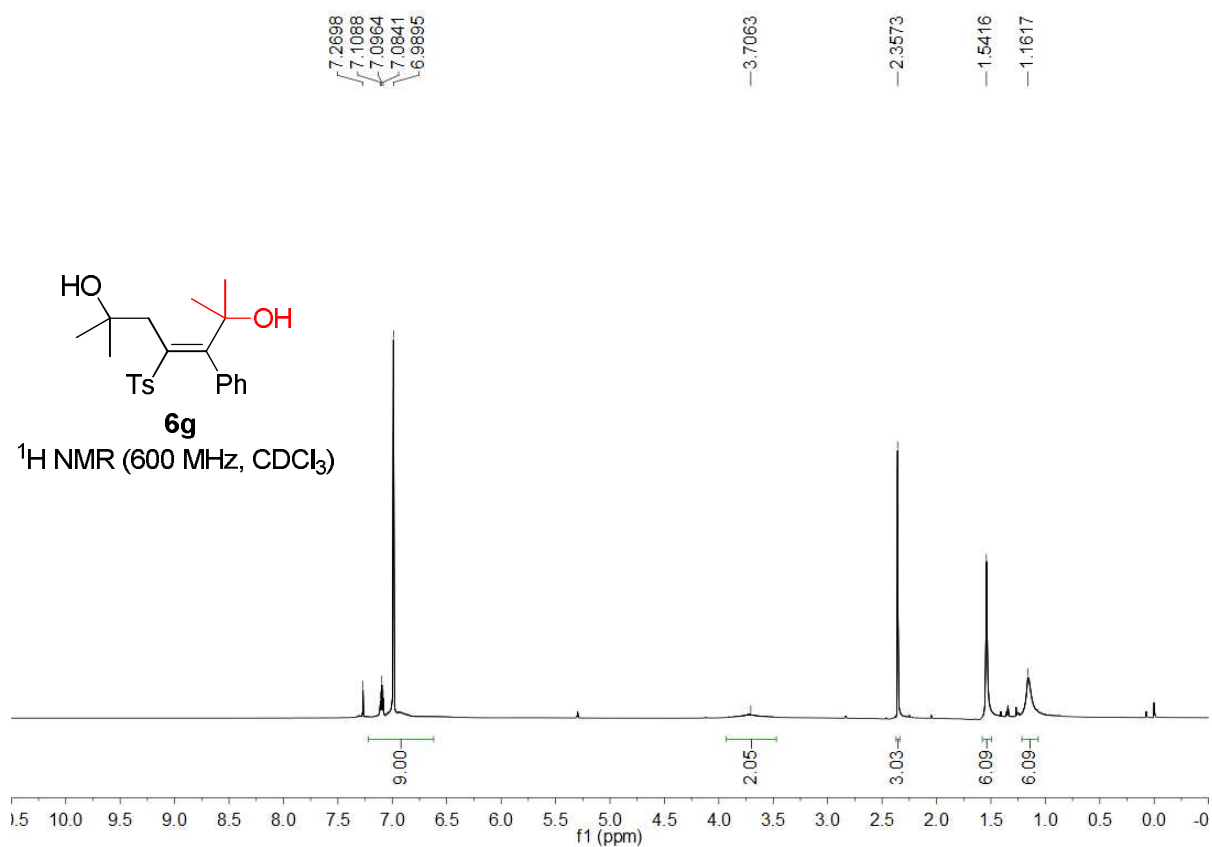


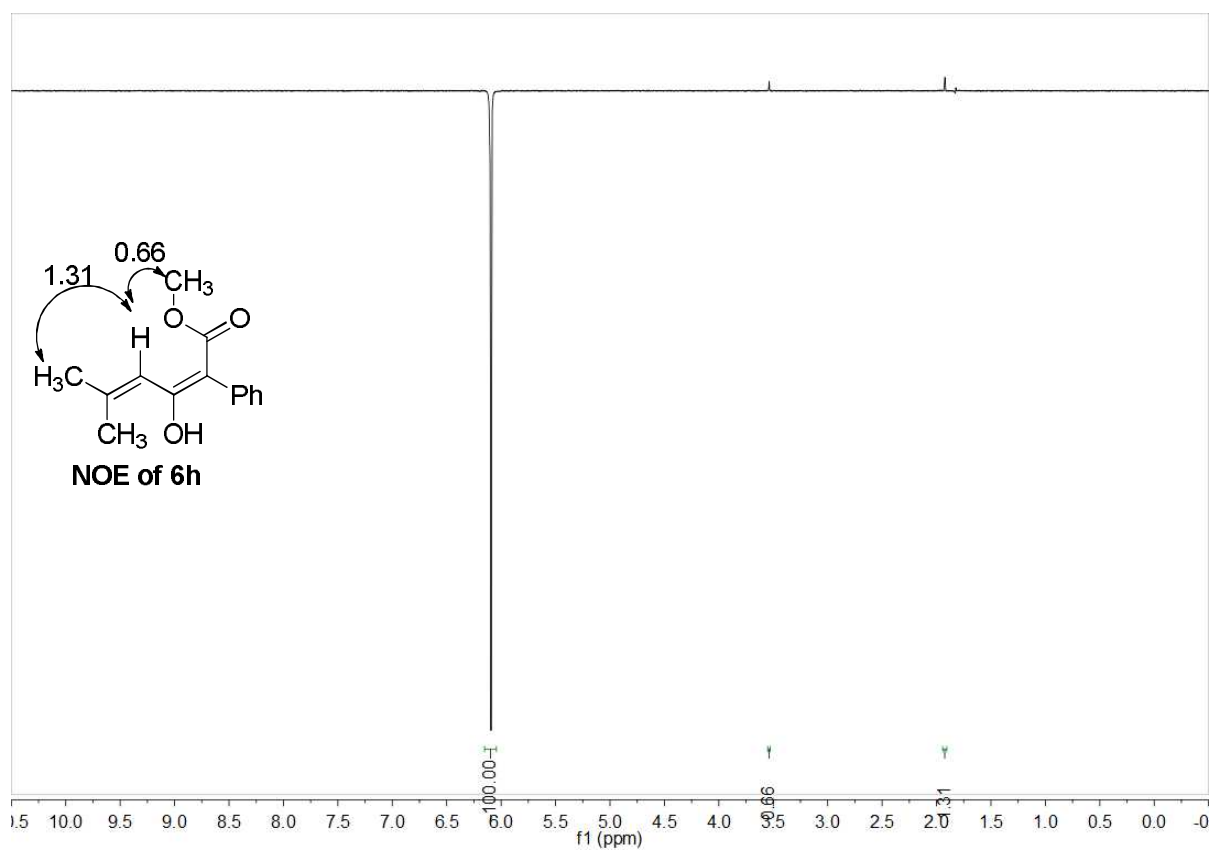
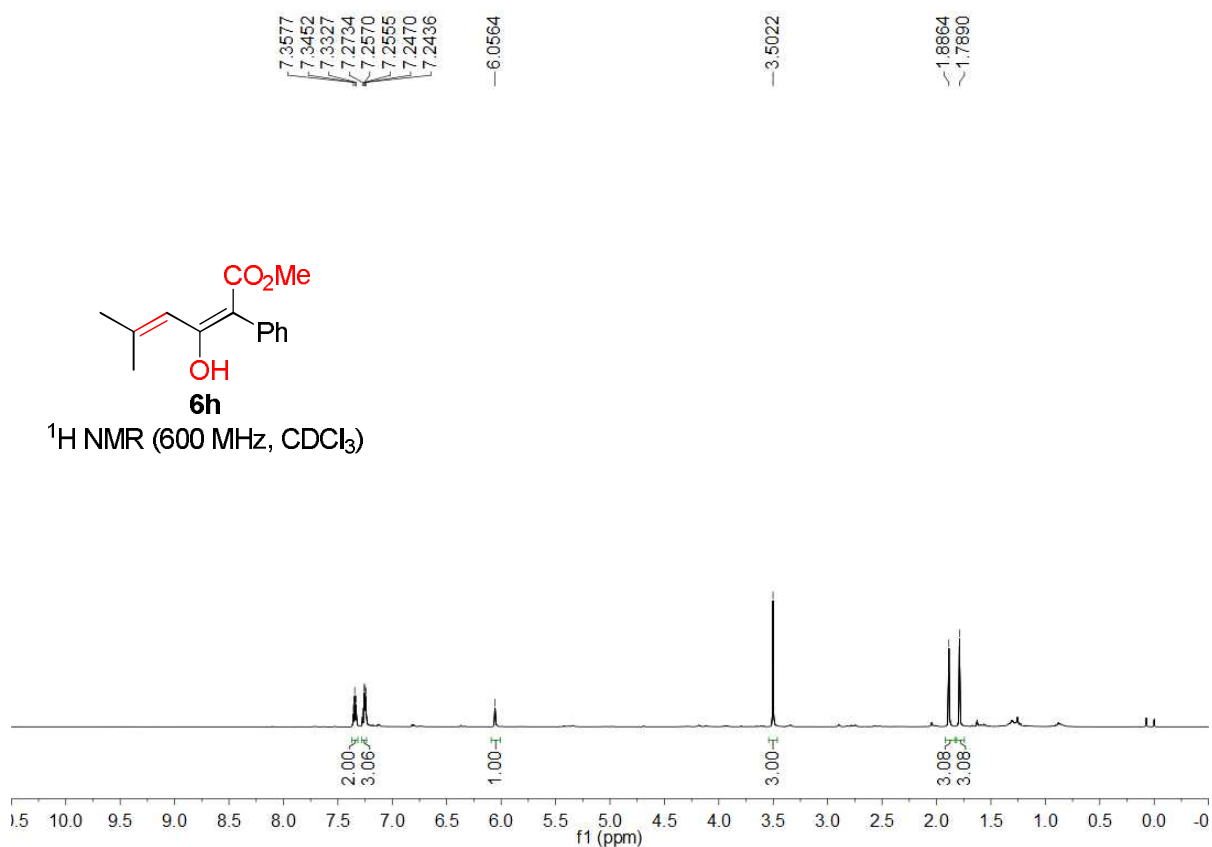
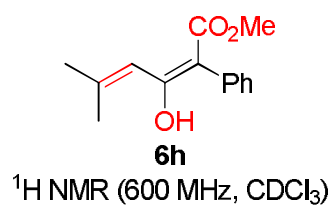


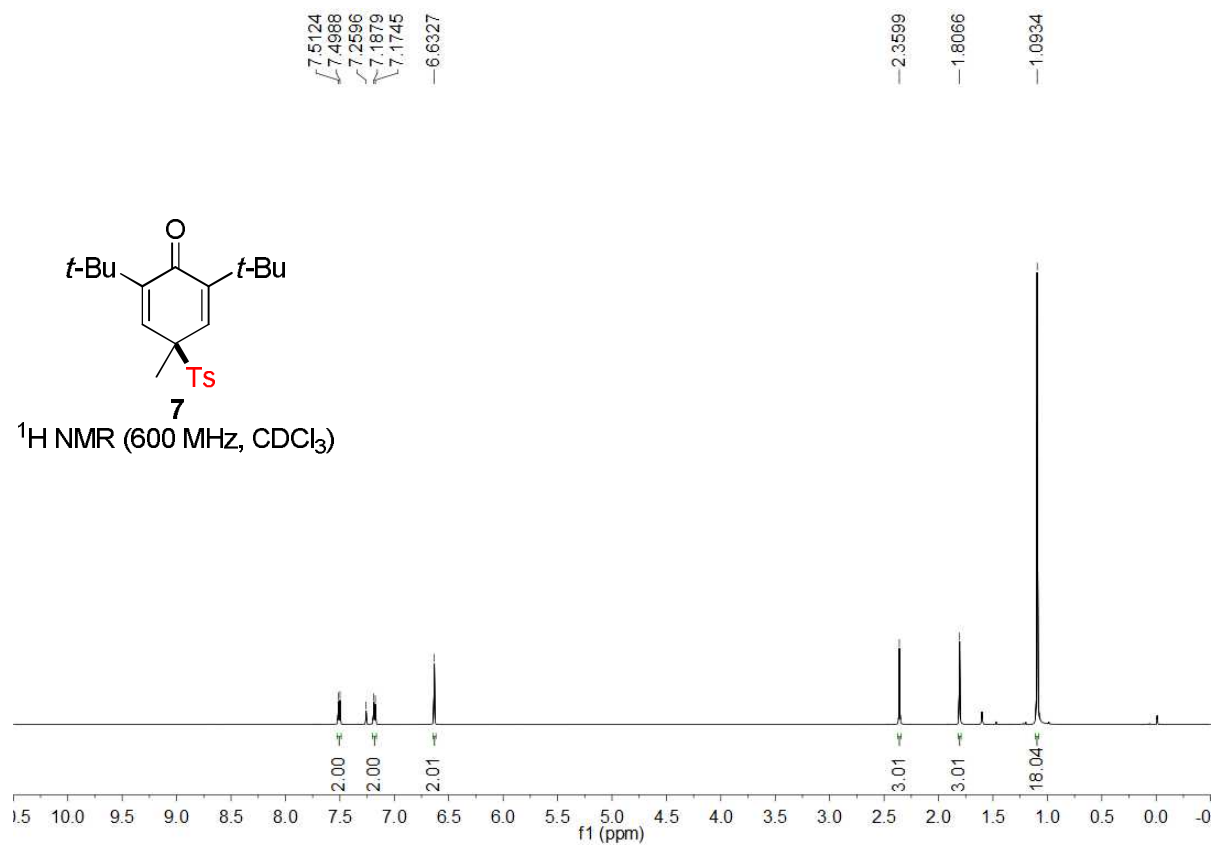
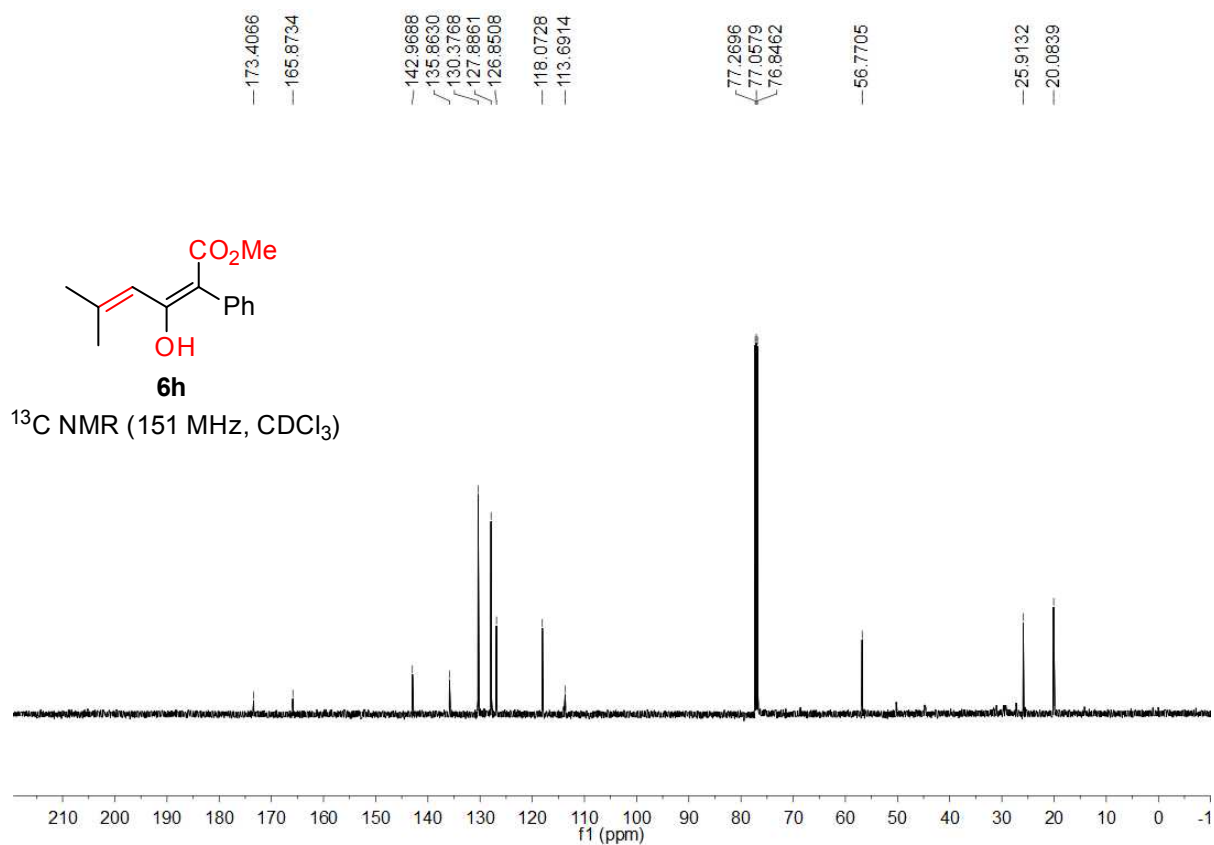


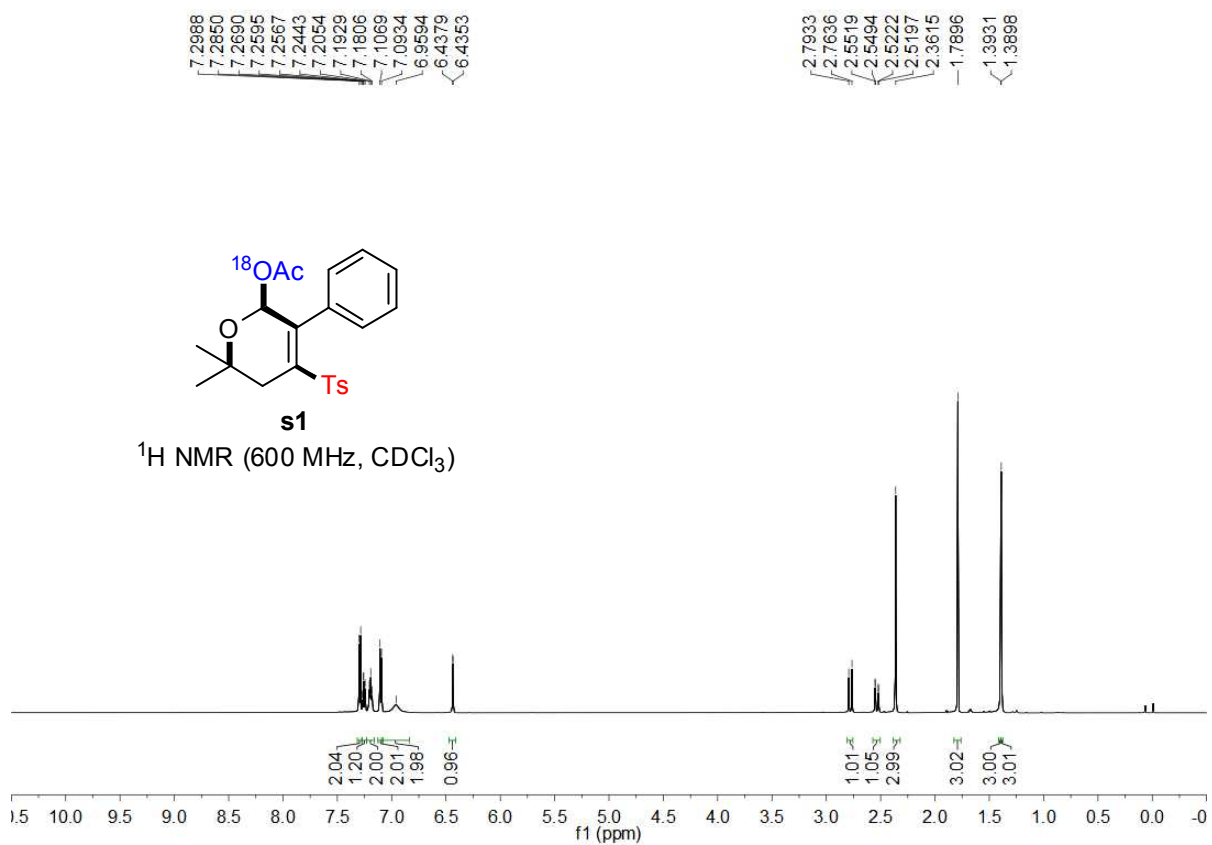
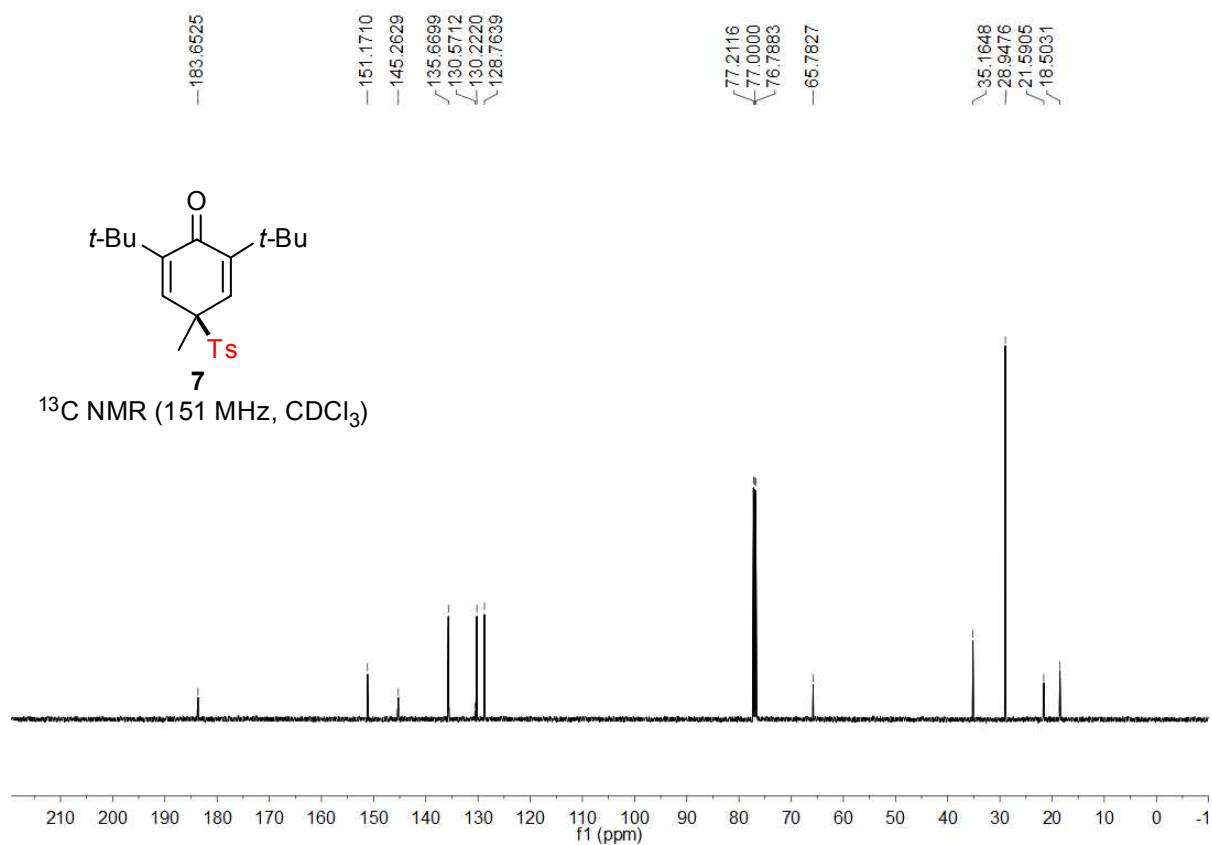


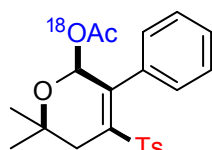






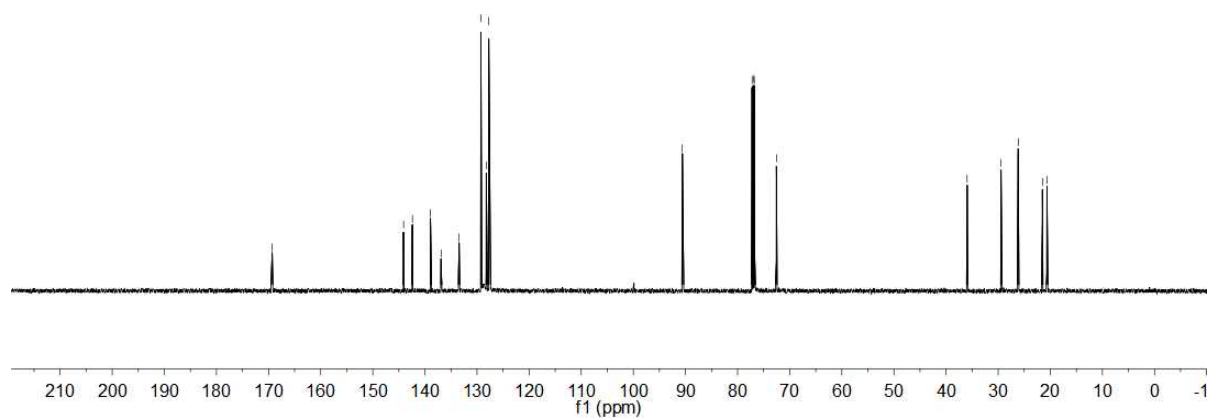






s1

^{13}C NMR (151 MHz, CDCl_3)



Checkcif Report of 3g

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: a_a

Bond precision: C-C = 0.0026 Å Wavelength=0.71073

Cell: a=5.8167(2) b=17.2043(6) c=19.0214(8)
 alpha=90 beta=91.831(2) gamma=90

Temperature: 250 K

	Calculated	Reported
Volume	1902.54(12)	1902.54(12)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Moiety formula	C21 H19 N O3 S	C21 H19 N O3 S
Sum formula	C21 H19 N O3 S	C21 H19 N O3 S
Mr	365.43	365.43
Dx, g cm ⁻³	1.276	1.276
Z	4	4
Mu (mm ⁻¹)	0.190	0.190
F000	768.0	768.0
F000'	768.83	
h,k,lmax	7,22,24	7,22,24
Nref	4367	4289
Tmin,Tmax	0.966,0.985	0.966,0.986
Tmin'	0.943	

Correction method= # Reported T Limits: Tmin=0.966 Tmax=0.986
AbsCorr = NONE

Data completeness= 0.982 Theta(max)= 27.481

R(reflections)= 0.0456(3717) wR2(reflections)= 0.1580(4289)

S = 1.115 Npar= 238

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT242_ALERT_2_C	Low	'MainMol' Ueq as Compared to Neighbors of	C00A Check
PLAT242_ALERT_2_C	Low	'MainMol' Ueq as Compared to Neighbors of	C00G Check

Alert level G

PLAT012_ALERT_1_G	No	_shelx_res_checksum Found in CIF	Please Check
PLAT019_ALERT_1_G		_diffn_measured_fraction_theta_full/*_max < 1.0	0.997 Report
PLAT066_ALERT_1_G		Predicted and Reported Tmin&Tmax Range Identical	? Check
PLAT720_ALERT_4_G		Number of Unusual/Non-Standard Labels	45 Note
PLAT941_ALERT_3_G		Average HKL Measurement Multiplicity	4.5 Low

0 ALERT level A = Most likely a serious problem - resolve or explain
0 ALERT level B = A potentially serious problem, consider carefully
2 ALERT level C = Check. Ensure it is not caused by an omission or oversight
5 ALERT level G = General information/check it is not something unexpected

3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
2 ALERT type 2 Indicator that the structure model may be wrong or deficient
1 ALERT type 3 Indicator that the structure quality may be low
1 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

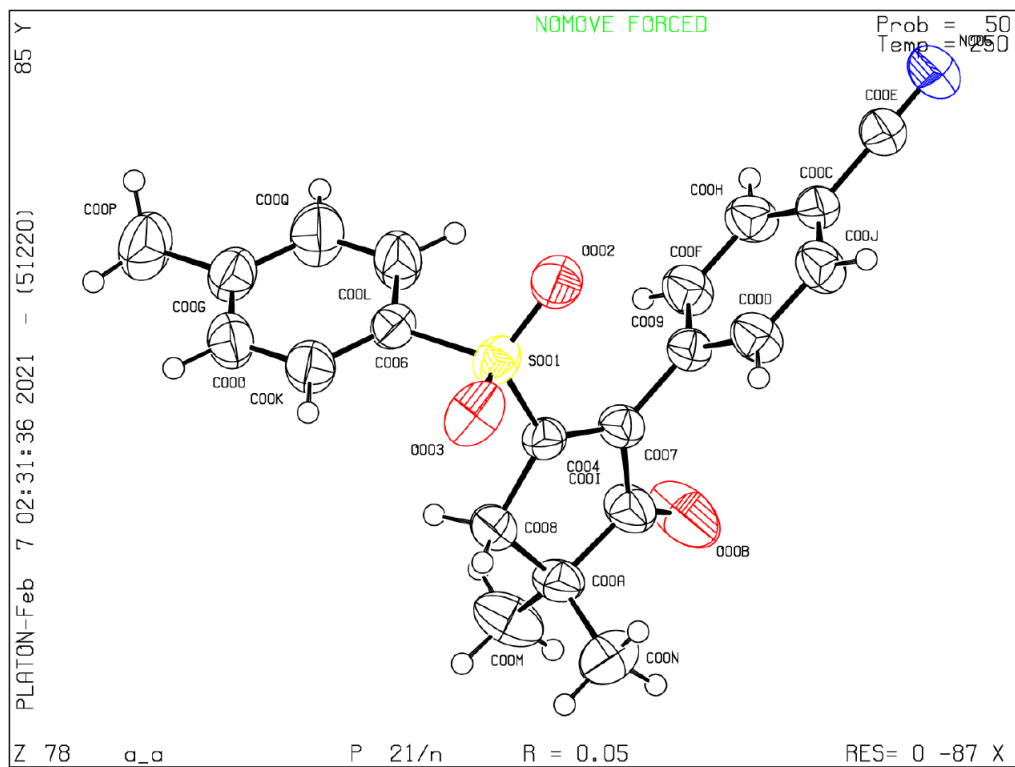
Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 05/12/2020; check.def file version of 05/12/2020



Checkcif Report of 5a

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: a_a

Bond precision: C-C = 0.0036 Å Wavelength=0.71073

Cell: a=10.8083(4) b=11.6866(6) c=14.3467(6)
 alpha=90 beta=90 gamma=90

Temperature: 250 K

	Calculated	Reported
Volume	1812.16(14)	1812.16(14)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C20 H20 O4 S	C20 H20 O4 S
Sum formula	C20 H20 O4 S	C20 H20 O4 S
Mr	356.42	356.42
Dx, g cm ⁻³	1.306	1.306
Z	4	4
Mu (mm ⁻¹)	0.200	0.200
F000	752.0	752.0
F000'	752.85	
h,k,lmax	14,15,18	14,15,18
Nref	4164 [2368]	4091
Tmin,Tmax	0.931,0.976	0.684,0.746
Tmin'	0.921	

Correction method= # Reported T Limits: Tmin=0.684 Tmax=0.746
AbsCorr = NONE

Data completeness= 1.73/0.98 Theta(max)= 27.510

R(reflections)= 0.0311(3815) wR2(reflections)= 0.0977(4091)

S = 1.151 Npar= 229

The following ALERTS were generated. Each ALERT has the format
test-name ALERT alert-type alert-level.
Click on the hyperlinks for more details of the test.

● **Alert level G**

PLAT012_ALERT_1_G	No	_shelx_res_checksum Found in CIF	Please Check
PLAT720_ALERT_4_G		Number of Unusual/Non-Standard Labels	45 Note
PLAT850_ALERT_4_G		Check Flack Parameter Exact Value 0.00 with s.u.	0.02 Check

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